On the combined effect of longitudinal diffusion and external mass transfer resistance in fixed bed operations

A. ACRIVOS

Department of Chemical Engineering, University of California, Berkeley, California

Abstract—This paper considers the combined effect of longitudinal diffusion and external mass transfer resistance on the performance of fixed bed processes with a favourable non-linear isotherm. It is shown that, whereas the linear additive principle is obeyed when the isotherms are "almost linear," for non-linear systems the two mechanisms are definitely not linearly additive. A simple method is proposed for estimating this combined effect with good accuracy.

Résumé—Cet article traite de l'effet combiné de la diffusion longitudinale et de la résistance externe au transfert de masse sur la performance des procédés utilisant un lit fixe avec isotherme non linéaire. Ce système n'obéit plus au principe additif linéaire quand les isothermes ne sont pas linéaires ou "presque linéaires." L'auteur propose une méthode simple pour prévoir l'effet combiné avec une bonne précision.

Zusammenfassung—In dieser Arbeit wird die Überlagerung einer longitudinalen Diffusion und eines äusseren Stoffübergangswiderstandes auf die Ausbeute eines Festbettprozesses besonders mit nichtlinearer Isotherme erörtert. Es wird gezeigt, dass bei "nahezu" linearer Isotherme das Prinzip der linearen Additivität erfüllt wird, während sich bei nichtlinearen Systemen die bieden Mechanismen sicherlich nicht linear addieren. Eine einfache Methode wird vorgeschlagen, die diesen, Effekt aus der Überlagerung mit guter Genauigkeit abzuschätzen gestattet.

INTRODUCTION

IT HAS long been recognized that external resistance to mass transfer, longitudinal diffusion, and the form of the equilibrium isotherm play an important role in determining the shape of the breakthrough curve for the standard fixed bed operations. It is understandable therefore that a considerable effort has been spent in an attempt to determine to what extent these factors affect the performance of fixed bed processes and under what conditions they must be taken into account in design calculations. The more noteworthy contributions on this subject have been recently reviewed in the comprehensive article by VERMEULEN [1].

Two general characteristics of breakthrough curves are of particular interest: the speed with which this chromatographic band travels along the column, and its relative width. It has already been established that the speed is a function primarily of the isotherm and can
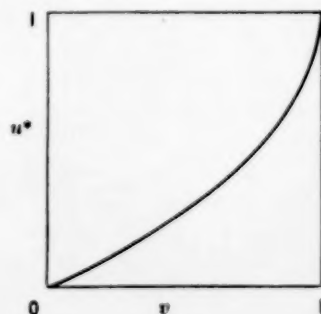

FIG. 1. General shape of the favourable isotherm.

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therefore be obtained with good accuracy from the equilibrium theory. On the other hand, for isotherms of the so-called favourable type (see Fig. 1) the relative width is not seriously affected by the form of the equilibrium curve, but is primarily a function of the finite rate of mass transfer and of longitudinal diffusion, if other usually secondary effects, intraparticle diffusion for example, are neglected.

Earlier studies, far too numerous to be mentioned here in detail, were concerned with the problem of determining to what an extent these two mechanisms, taken separately, were responsible for the band spread often observed in chromatographic and ion-exchange columns. It appears, however, that for some processes the effects of a finite rate of mass transfer and longitudinal mixing are comparable, which therefore raises the interesting question of how these two mechanisms combine. Are the effects linearly additive, as has been sometimes postulated, or is the physical phenomenon far too complicated for such a simple solution ?

This problem was recently investigated by KLINKENBERG et al. [2,3] who restricted themselves to a linear isotherm. By simplifying a rather general mathematical solution first obtained by AMUNDSON and LAPIDUS [4] these authors were able to prove that indeed the two mechanics of longitudinal diffusion and gas-phase mass transfer resistance are exactly additive and that quantities such as the H.E.T.P. have the linear additive property. The same result was also obtained from a statistical model [2] under the assumption that the two mechanisms are statistically independent.

These conclusions reached by KLINKENBERG et al. apply of course only to dilute solutions for which the isotherms may be assumed linear, and one would certainly not expect that for non-linear systems the two mechanisms would act independently. The purpose of this note therefore is to pursue this study somewhat further and consider the combined effects of longitudinal diffusion and external mass transfer resistance on the performance of fixed bed processes for non-linear isotherms of the favourable type. As will be shown, this problem admits of a relatively simple mathematical solution.

SOLUTIONS FOR FAVOURABLE BASIC EQUATIONS AND THEIR ISOTHERMS

According to the well-known basic equations for a one-dimensional fixed bed process,

$$D \frac{\partial^2 c}{\partial X^2} = U \frac{\partial c}{\partial X} + \epsilon \frac{\partial c}{\partial t} + (1 - \epsilon) \frac{\partial q}{\partial t} \qquad (1)$$

and

$$\frac{\partial q}{\partial t} = k [c - c^*(q)] \qquad (2)$$

if isothermal conditions are assumed, and if effects other than those caused by longitudinal mixing and by a finite rate of external mass transfer are neglected. The symbols have the following meaning :

$c =$ concentration in moles per unit volume of absorbate in the moving stream.

$q =$ concentration in moles per unit volume of the stationary phase.

$D =$ the combined molecular and eddy longitudinal diffusion coefficients.

$\epsilon =$ the fractional void volume of the bed.

$U =$ the superficial velocity of the fluid through the bed.

$k =$ a mass transfer coefficient with reciprocal time units.

$c^*(q) =$ the equilibrium value of c corresponding to a given stationary phase concentration q.

$X =$ distance along the axis of the bed.

$t =$ the time

and the boundary conditions will be taken, for simplicity, as

$c = c_0$ and $q = Q$ for $X \to - \infty$ where $c^*(Q) = c_0$.

$c = 0 = q$ for $X \to + \infty$.

$c = c_0 H(- X)$ at $t = 0$.

where $H(z)$ is the Heaviside step function such that $H(z) = 0$ for $z < 0$ and $H(z) = 1$ for $z > 0$.

As might be expected, a complete solution of equations (1) and (2) has not yet been discovered, except for the special case of a linear isotherm [3, 4]. It was first noticed by SILLÉN and EKEDAHL [5] however, that in the absence of

longitudinal diffusion ($D = 0$) and for an isotherm of the so-called favourable type (Fig. 1) where

$$\frac{d^2 c^*}{dq^2} > 0 \quad \text{for all } q \geqslant 0 \tag{3}$$

the breakthrough curve approaches a constant pattern as it moves down the column. A similar result was recently reached by LIGHTFOOT [6] for the case of an infinite rate of mass transfer but a non-zero longitudinal diffusion coefficient. Of course, the constant pattern is only an asymptotic profile which is strictly speaking attained only at distances far removed from the entrance of the column. Yet it has been established by LAPIDUS and ROSEN [7] that, as is often the case for analogous physical problems, such a constant pattern is quickly reached inside the bed and may therefore be used in design calculations with good accuracy, unless the column is very short.

It is easy to show now that c and q become asymptotically functions of a single variable, if the isotherm is of the favourable type. Thus, if

$$z \equiv \left[X - \frac{U c_0 t}{\epsilon c_0 + (1 - \epsilon) Q} \right] \frac{U (1 - \epsilon) Q}{D \left[\epsilon c_0 + (1 - \epsilon) Q \right]} \tag{4}$$

then, asymptotically, equations (1) and (2) reduce respectively to

$$\frac{d^2 u}{dz^2} = \frac{du}{dz} - \frac{dv}{dz}$$

which can immediately be integrated into

$$\frac{du}{dz} = u - v \tag{5}$$

and

$$\alpha \frac{dv}{dz} = u^* (v) - u \tag{6}$$

Therefore

$$\alpha \frac{dv}{du} = \frac{u^* (v) - u}{u - v} \tag{7}$$

with

$$u = \frac{c}{c_0}, \quad v = \frac{q}{Q} \quad \text{and} \quad u^* (v) = \frac{c^* (vQ)}{c_0} \tag{8}$$

These equations also must satisfy the boundary conditions

$$u = v = 1 \quad \text{at} \quad z = -\infty$$
$$u = v = 0 \quad \text{at} \quad z = \infty$$

and by definition,

$$u = \tfrac{1}{2} \text{ at } z = 0 \tag{9}$$

We see then that the dimensionless group α, defined as

$$\alpha \equiv \left[\frac{UQ}{\epsilon c_0 + (1 - \epsilon) Q} \right]^2 \frac{1 - \epsilon}{Dk} \tag{10}$$

plays indeed a very significant role in the performance of fixed bed operations and measures in a sense the relative importance of longitudinal diffusion and external mass transfer resistance in causing band spreading.

Again, a closed form analytic solution of equations (5) and (7) cannot, unfortunately, be obtained for an arbitrary isotherm $u^* (v)$ unless $\alpha \to 0$ or ∞.

For $\alpha \to 0$, $u = u^* (v)$, and therefore

$$z = \int_u^{1/2} \frac{du}{v^* - u} \quad \text{where} \quad u^* (v^*) = u \tag{11}$$

as obtained by LIGHTFOOT [6]. On the other hand, if $\alpha \to \infty$, $u \to v$, and

$$\frac{z}{\alpha} = \int_u^{1/2} \frac{du}{u^* (u) - u} \tag{12}$$

However, for intermediate values of α, a numerical integration of the equations is indicated. Nevertheless, it is possible to arrive at an approximate solution, perfectly adequate for most applications, by elementary methods.

Approximate solutions

Let

$$u^* (v) \equiv rv + g (v) \tag{13}$$

where r is equal to the slope of the isotherm at $v = 0$,

and

$$v \equiv au + v_1 (u) \tag{14}$$

so that $g (0) = g' (0) = v_1 (0) = v_1' (0) = 0$. Upon substitution in equations (5) and (7) one readily finds that

$$a = \frac{1}{2} \left\{ 1 - \frac{r}{\alpha} + \sqrt{\left[\left(1 - \frac{r}{\alpha} \right)^2 + \frac{4}{\alpha} \right]} \right\} \tag{15}$$

and that

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$$-\frac{du}{dz} = (a-1)u + v_1(u) \qquad (16)$$

Therefore, since by definition $u = \frac{1}{2}$ when $z = 0$,

$$z = \int_u^{0.5} \frac{du}{(a-1)u + v_1(u)} = \frac{1}{(a-1)} \ln \frac{1}{2u} -$$
$$- \frac{1}{a-1} \int_u^{0.5} \frac{v_1}{(a-1)u^2 + uv_1} du \qquad (17)$$

In particular, if $u \to 0$

$$z = \frac{2}{\left\{ \sqrt{\left[\left(1-\frac{r}{\alpha}\right)^2 + \frac{4}{\alpha}\right]} - \left(1 + \frac{r}{\alpha}\right)\right\}} \left[\ln\frac{1}{2u} + A\right] \qquad (18)$$

where

$$A \equiv - \int_0^{0.5} \frac{v_1}{(a-1)u^2 + uv_1} du \qquad (19)$$

Of course, an entirely similar solution can be obtained for $u \to 1$. However, since one is in general interested primarily in the distance z between the midpoint of the breakthrough curve ($u = 1/2$) and a small value of u, $u = 0.05$ say, equation (15) is usually quite adequate. The constant A can be determined accurately only by either a numerical solution of equations (7) and (19), or by a series expansion. Fortunately, though, a fairly reliable estimate of A can be arrived at by considering its asymptotic forms for some typical isotherms and then interpolating between the two extremes.

THE PARAMETER A FOR A CONSTANT EXCHANGE FACTOR

For a constant exchange factor, the equilibrium isotherm becomes

$$u^*(v) = \frac{rv}{1 - (1-r)v} \qquad (20)$$

where $r < 1$ if the isotherm is favourable. Equations (5) and (7) can then immediately be solved for the extremes $\alpha \to 0$ and $\alpha \to \infty$. Thus,

(a) For $\alpha \to 0$

$$z = \frac{1}{1-r} \ln \frac{2(1-u)}{(2u)^r}$$

and therefore

$$A \to \frac{\ln 2}{r} \text{ as } \alpha \to 0 \qquad (21)$$

(b) For $\alpha \to \infty$

$$z \to \frac{\alpha}{1-r} \ln \frac{[2(1-u)]^r}{2u}$$

so that

$$A \to r \ln 2 \text{ as } \alpha \to \infty. \qquad (22)$$

For intermediate values of α, a simple interpolation formula can readily be obtained. One notes from equation (15) that the two mechanisms have a comparable effect on the overall solution where $r \simeq \alpha$, and it appears reasonable therefore to expect that

$$\frac{\ln 2}{A} \simeq \frac{1}{1 + (\alpha/r)} \left\{\frac{\alpha}{r^2} + r\right\} \qquad (23)$$

which reduces to equations (21) and (22) as $\alpha \to 0$ and $\alpha \to \infty$ respectively. It should be remarked here that formulae similar to that given by equation (23) are not infrequently used in physical problems to interpolate between two exact asymptotic expressions, and that the interpolation formula chosen here is therefore not as arbitrary as it might appear at first glance. It is seen from Table 1 moreover that the agreement between an exact numerical solution for $r = 1/2$ and equation (23) is indeed excellent.

Table 1. A comparison of the exact values of A for $r = \frac{1}{2}$ and those calculated from equation (23).

α	A (exact)	A from eqn. (23)
0	1·39	1·39
$\frac{1}{8}$	0·87	0·87
$\frac{1}{2}$	0·54	0·56
1	0·44	0·46
2	0·38	0·41

As a point of interest we might mention here that as $r \to 1$, an exact solution may be arrived at without difficulty. Thus, in the limit as $r \to 1$,

$$\frac{(1-r)z}{1+\alpha} = \ln \frac{2(1-u)}{2u} \qquad (24)$$

for all α, which clearly shows that the two mechanisms of longitudinal diffusion and external mass transfer resistance are indeed linearly additive for " almost linear systems " only. A similar conclusions would of course be reached for a system with any " almost linear " isotherm.

Naturally, a similar approach can also be used successfully for other isotherms. In general the two extreme cases ($\alpha \to 0$, or $\alpha \to \infty$) can be solved directly without too much effort, and the interpolation formula, equation (23), would be expected to hold with a fair degree of accuracy. It is believed for example that such an approach could be used to investigate the effect of longitudinal diffusion on the behaviour of a chromatographic column with the rather commonly employed " Thomas-type " kinetic law [8, 9].

THE IRREVERSIBLE BREAKTHROUGH ($r = 0$)

Equation (23) appears to be accurate for $1/4 < r < 1$. As however the irreversible case, $r \to 0$, is approached, a different solution is required. Fortunately though the equations can be solved exactly for this special but rather important problem. Thus, if

$$u^* (v) = 0 \text{ for } 0 < v < 1$$

and

$$u^* = u \text{ for } v = 1$$

it can be shown by elementary means that:

(a) If $\lambda \geqslant 1$, where $\lambda \equiv \frac{1}{2} \left\{ \sqrt{\left(1 + \frac{4}{\alpha}\right)} - 1 \right\}$ (25)

$$z = \ln 2 (1 - u) \text{ for } z \leqslant \ln \frac{2\lambda}{\lambda + 1} \quad (26)$$

and

$$z = \frac{1}{\lambda} \left[\ln \frac{1}{2u} + \lambda \ln \frac{2\lambda}{\lambda + 1} + \ln \frac{2}{1 + \lambda} \right]$$

$$\text{for } z \geqslant \ln \frac{2\lambda}{\lambda + 1} \quad (26a)$$

(b) If on the other hand $\lambda \leqslant 1$, then

$$u = 1 - e^z \frac{\lambda + 1}{2\lambda} \left\{ 1 - \frac{1}{2} \left(\frac{\lambda + 1}{2\lambda} \right)^\lambda \right\}$$

$$\text{for } z \leqslant \ln \frac{2\lambda}{\lambda + 1} \quad (27)$$

and

$$z = \frac{1}{\lambda} \ln \frac{1}{2u} \text{ for } z \geqslant \ln \frac{2\lambda}{\lambda + 1} . \quad (27a)$$

We easily see therefore from equations (18), (26a) and (27a) that, when $r = 0$,

$$A = \lambda \ln \frac{2\lambda}{\lambda + 1} + \ln \frac{2}{1 + \lambda} \text{ for } \lambda \geqslant 1 \quad (28)$$

$$A = 0 \text{ for } \lambda \leqslant 1$$

It might be worth remarking here that an analytic solution similar to that shown above, can also be readily obtained for an isotherm of the form

$$u^* (v) = rv \text{ for } v \leqslant 1$$

$$u^* = u \text{ for } v = 1.$$

This solution will however not be reported here since such isotherms do not appear to be very realistic.

CONCLUSIONS

A simple procedure has been presented for estimating with good accuracy the combined effect of longitudinal diffusion and external mass transfer resistance on the performance of fixed bed processes with a non-linear but favourable isotherm. This analysis shows that the linear additive principle is obeyed when the isotherm is " almost linear " but that for non-linear systems the two mechanisms are definitely not linearly additive and must be taken into account by means of equations (18) and (23) for $\frac{1}{4} < r < 1$, and equation (27) for $r \to 0$. It appears, therefore, that conclusions arrived at by a study of linear problems about the way in which the different mechanisms combine in fixed bed operations should not be automatically extended to non-linear processes, without at least some additional work.

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Study on cooler condensers for gas–vapour mixtures

T. Mizushina, M. Nakajima* and T. Oshima†

Kyoto University, Kyoto, Japan

Abstract—The graphical method for the design of cooler condensers by Mizushina *et al.* presented in a previous paper is revised.

Furthermore gas–vapour mixtures, such as water–air, benzene–air, toluene–air and methanol–air were cooled in a vertical single tube condenser, and the experimental data were found to be in good agreement with the results of calculation by the method of this paper.

Résumé—Les auteurs révisent la méthode graphique de calcul de condenseurs de Mizushina et Col. déjà publiée.

De plus des mélanges gaz–vapeur tels que eau–air, benzène–air, toluène–air et méthanol–air sont refroidis dans un condenseur à tube vertical unique, et les données expérimentales sont en bon accord avec les résutlats des calculs obtenus par la méthode donnée.

Zusammenfassung—Die graphische Methode zur Planung von Kühler-Kondensatoren, die von Mizushina u.a. in einer früheren Arbeit veröffentlicht worden war, wurde überarbeitet.

Weitere Gas-Dampf-Gemische, wie Wasser–Luft, Benzol–Luft, Toluol–Luft und Methanol–Luft wurden in einem vertikalen Einrohrkondensator gekühlt. Die experimentellen Ergebnisse stimmen mit den nach der Methode dieser Arbeit errechneten Ergebnissen gut überein.

Introduction

Since the stepwise method for designing cooler condensers was published by Colburn and Hougen [1] various design methods have been proposed by Bras [2, 3, 4], Cribb and Nelson [5] and Huldén [6]. These papers described methods of calculation without experimental data. Cairns [7] presented the experimental results of the water–air and chloroform–air systems, and Smith and Robson [8] the experimental data of the benzene–air system. In both papers the experimental results were compared with those of Colburn and Hougen's method.

Recently, Mizushina *et al.* [9] published a graphical design method for cooler condensers, which was applicable to any gas–vapour mixture system. In this previous paper even in the case of mixtures having high vapour concentration, it was assumed that $h_g/k_g = C_s$ for water–air system and that $p_{BM} (P - p_i) = 1$ for mixtures other than the water–air system. These assumptions however sometimes cause considerable error in estimating heat transfer surface area.

In this paper a more accurate method involving some additional procedures will be developed, and the results of the calculation will be shown to be in good agreement with the experimental data obtained for four systems, i.e. water–air, benzene–air, toluene–air and methanol–air in a single tube cooler condenser.

Experimental Apparatus and Procedure

The apparatus consists principally of a boiler for the liquids, a vertical single tube condenser, a condensate receiver, an air compressor and a cooling water pump.

Air was pumped by a ¼ h.p. compressor through a CaCl$_2$ column for drying and heated electrically before being mixed with the vapour. Its flow rate was controlled by a valve and measured with an

* Present address : Himeji Technical College.
† Present address : Kimura Entetsu Chemical Plant Co. Ltd.

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orifice meter. Various kinds of liquids were
evaporated in the boiler and mixed into the air
flow. The boiler had an internal capacity of 30 cm
diameter × 40 cm height, being heated with two
2 kW immersion heaters. The electric power input
was controlled by a variac, and measured by an
ammeter and a voltmeter. The vapour rate was
measured by the power input. Power input vs.
the rate of evaporation of liquid was calibrated
beforehand. The heat loss from the boiler was
obtained as 1·59 Δt kcal/hr, where Δt °C was the
temperature difference between boiling liquid
temperature and the surrounding air tempera-
ture. In the case of the high vapour content
water–air system an auxiliary boiler was used to
produce the additional vapour. The gas–vapour
mixture was led to the condenser through a
¾ in. steel pipe.

The condenser was a vertical double-tube type.
The gas–vapour mixture flowed downwards inside
the inner tube, and the cooling water flowed
countercurrently in the annulus. The inner tube
was made of copper and of 29 mm o.d., 23 mm
i.d. and the length of the tube exposed to the
cooling water was 180 cm, i.e. the effective internal
surface area was 0·130 m². A 100 cm long
calming section was provided before the condenser
and a 20 cm long section was extended below the
bottom of the condenser. The external tube
forming the water jacket was 2 in. Esron
(polyvinylchloride resin) pipe (i.d. 50 mm).

The condensate was received in the condensate
receiver, which was attached to the bottom of the
copper tube. The rate of condensation was
determined directly from the weight of the con-
densate collected during a known time.

The cooling water was pumped by a ½ h.p.
turbine pump and metered with an orifice meter.

Calibrated copper–constantan thermocouples
were located at the inlet and outlet of the cooling
water, the air line before entering the vapour
line, the inlet and outlet of the gas–vapour
mixture and also at ten points located at equal
intervals on the axis of the inner tube of the
condenser. Thermocouples were also set on the
wall of the inner tube and midway between the
annulus walls at heights corresponding to those
on the axis. Thus the change in the temperature

of the gas–vapour mixture, the pipe wall and the
cooling water were measured. The electrical
potential was measured by a potentiometer
within an accuracy of 1 μV which corresponds to
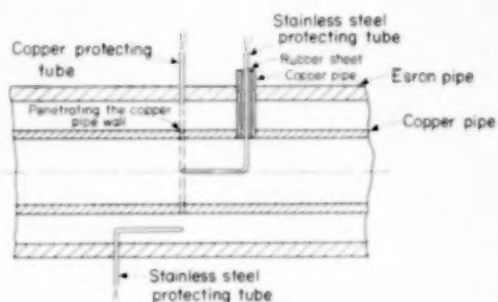about 0·03 °C. The setting of the thermocouples
is shown in Fig. 1.

Fig. 1. Details of setting of thermocouples.

The boiler was insulated with 5 cm thick
diatomaceous earth and all air lines and gas–
vapour mixture lines were lagged with 2 cm thick
glass wool.

In making each run the boiler was filled with
liquid, the power input to the boiler was set at
the required vaporization rate and air was intro-
duced into the vapour line.

Sufficient stabilizing time was allowed for each
run. At steady state conditions, the temperature
at each point, the power input to the boiler and
the rates of air, vapour, condensate and cooling
water were measured. The results of the experi-
ments are listed in Table 1.

METHOD OF CALCULATION

Since the publication of the previous paper [9]
on the design of cooler condensers for gas–vapour
mixtures the authors have calculated the heat
transfer surface area for many different cases,
and it was found that the assumptions that
$h_g/k_g' = C_s$ for mixtures of water vapour and air
and $p_{BM}/(P - p_i) = 1$ for mixtures other than
the water–air system sometimes caused consider-
able error in estimating the surface area. In
order to improve the accuracy of the graphical
method the following additional calculation
procedures were developed.

Table 1. Summary of experimental data

System	Run No.	Vapour rate (kg/hr)	Air rate (kg/hr)	Cooling water rate (kg/hr)	Condensate* (kg/hr)	Gas-vapour temperature (°C)		Cooling water temperature (°C)	
						gas inlet	gas outlet	water inlet	water outlet
Water–air	1	16·42	3·22	1445	15·34 (15·54)	97·9	69·8	8·5	14·8
	2	5·93	3·44	1458	5·69 (5·69)	99·9	52·1	8·2	10·6
	3	3·03	3·34	1363	2·84 (3·04)	100·2	43·0	9·2	10·6
	4	1·39	3·33	1470	1·28 (1·33)	98·2	32·6	9·6	10·2
Benzene–air	11	19·02	3·39	1518	15·50 (16·21)	77·2	43·6	10·4	11·8
	12	10·07	3·39	1468	8·04 (8·20)	66·8	33·2	10·7	11·4
	13	2·36	3·39	1468	1·43 (1·36)	59·5	18·9	10·7	10·9
Toluene–air	21	20·93	3·36	1521	17·02 (17·57)	101·1	64·8	13·6	15·0
	22	7·02	3·33	1521	6·38 (6·44)	97·8	46·4	14·0	14·5
	23	2·15	3·33	1521	1·58 (1·62)	91·8	30·7	14·1	14·3
Methanol–air	31	9·79	3·36	977	7·01 (7·90)	61·5	40·0	12·5	14·7
	32	4·66	3·36	982	3·68 (3·73)	62·9	30·3	12·5	13·6
	33	0·98	3·36	973	0·53 (0·41)†	70·3	20·4	12·4	12·6

* The values in parentheses in this column were obtained from a material balance assuming that the gas mixture was saturated at the outlet.

† Since the outlet gas of Run No. 33 was not saturated the calculated value differs considerably from the observed value.

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Basic equations

For the sake of convenience the important basic equations presented in the previous paper [9] will be noted again here. The equations are numbered to agree the numbering in the previous paper [9].

The ratio of the heat and mass transfer coefficient is

$$\frac{h_g}{k_g'} = \alpha C_s \qquad (3)$$

where

$$\alpha = \frac{p_{BM}}{P - p_i} \left(\frac{Sc}{Pr}\right)^{\frac{1}{3}} \qquad (4)$$

$$h_g = j \, C_g \, G' / (Pr)^{\frac{2}{3}}. \qquad (12)$$

The enthalpy balance is

$$- G_B \, di_g = \frac{h_g}{\alpha \, C_s} (i_g' - i_i') \, dA \qquad (6')$$

where i' is the " modified enthalpy " and is defined as

$$i_g' = \alpha \, C_s \, t_g + \lambda_0 \, H_g \qquad (7')$$

Therefore

$$A = \alpha \, G_B \int_{i_{g2}}^{i_{g1}} \frac{C_s \, di_g}{h_g (i_g' - i_i')} \qquad (8')$$

Deriving

$$\frac{h_g}{C_s} = \frac{h_B}{\beta \, C_B} \qquad (19)$$

where

$$\beta = (1 + H_g)^n \qquad (20)$$

equation (8') becomes

$$A = \frac{\alpha \, C_B \, G_B}{h_B} \int_{i_{g2}}^{i_{g1}} \frac{\beta \, di_g}{i_g' - i_i'} \, . \qquad (21')$$

A heat balance yields the slope of the operating line

$$\frac{di_g}{dt_l} = \frac{L \, C_l}{G_B} \qquad (9)$$

The slope of the path line of the gas–vapour mixture is

$$\frac{di_g}{dt_g} = \frac{1}{\alpha} \frac{i_g' - i_i'}{t_g - t_i} \qquad (10')$$

and the slope of the tie line is

$$\frac{i_g' - i_i'}{t_l - t_i} = - \frac{\alpha \beta \, h_0 \, C_B}{h_B} \qquad (22')$$

The difference between the enthalpy and the modified enthalpy is given by

$$i_g' - i_g = (\alpha - 1) \, C_s \, t. \qquad (23)$$

The additional procedures

(1) Assuming that the mixture is saturated at the exit, calculate the values of β at the inlet and exit.

(2) Taking as a first approximation $\alpha = 1$, i.e. $h_g/k_g' = C_s$, construct tie lines of slope $- \beta \, h_0 \, C_B / h_B$ through the points A and Z on the operating line and locate A''' $(t_{iA'''}, i_{iA'''})$ and Z''' $(t_{iZ'''}, i_{iZ'''})$ on the saturation curve as shown in Fig. 2.
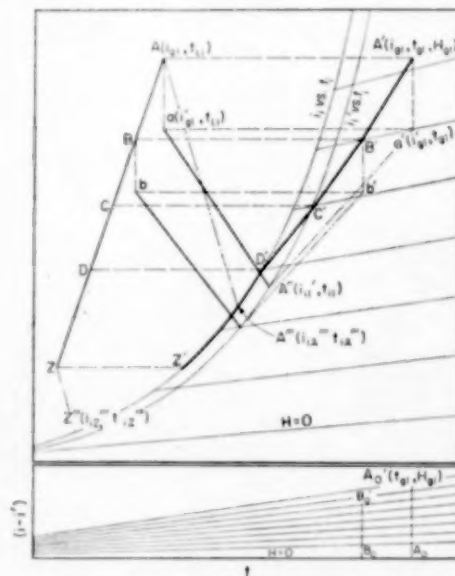

Fig. 2.   Enthalpy and modified enthalpy–temperature chart.

(3) Calculate the value of $\alpha_{A'''}$ and $\alpha_{Z'''}$ by equation (4) using values of $p_{iA'''}$ and $p_{iZ'''}$ which correspond to $t_{iA'''}$ and $t_{iZ'''}$ respectively.

(4) Take the arithmetic mean value of $\alpha_{A'''}$ and $\alpha_{Z'''}$ for α. Usually, the value of α is less than one.

(5) Using the value of α obtained, follow the procedure in the previous paper [9].

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THE COMPARISON OF RESULTS OF CALCULATION AND EXPERIMENT

The procedure mentioned above was applied to all of the experimental runs. An example of such a calculation is given in the following section.

Run No. 1 (water–air system)

At the gas inlet:

$$H_g = 5\cdot10 \qquad \text{kg/kg of dry air}$$
$$C_g = 0\cdot418 \qquad \text{kcal/kg °C}$$
$$Pr = 0\cdot95$$
$$G' = 47200 \qquad \text{kg/m}^2 \text{ hr}$$
$$Re = 20970$$

Since the preliminary experiments on the heat transfer coefficient of this apparatus gave

$$j = 0\cdot0322 \, Re^{-0\cdot2},$$
$$j = 0\cdot0044$$

Substituting these values into equation (12) the heat transfer coefficient of the gas film h_g is calculated as

$$h_g = (0\cdot0044)(0\cdot418)(47200)/(0\cdot95)^{\frac{2}{3}} =$$
$$89 \text{ kcal/m}^2 \text{ hr °C}$$

The value of C_s obtained from Fig. 1 in the previous paper [9] is

$$C_s = 2\cdot55 \text{ kcal/kg of dry air °C}$$

Since the gas flows inside the tube $n = 0\cdot2$ in Fig. 1 in the reference [9]. Thus the value of β is obtained as,

$$\beta = 1\cdot436$$

From equation (19)

$$\frac{C}{h_B} = \frac{C_s}{\beta h_g} = \frac{2\cdot55}{(1\cdot436)(89)} = 0\cdot0200$$

Since the heat transfer coefficient of the cooling water was found to be 6900 kcal/m² hr °C in the preliminary experiments, and since the vapour film coefficient is calculated as 3260 kcal/m² hr °C from Nusselt's equation, the value of the combined conductance is

$$h_0 = 2210 \text{ kcal/m}^2 \text{ hr °C}$$

Since the gas condition at the inlet is $t_g = 97\cdot9$ °C, $H_g = 5\cdot10$ kg/kg of dry air, the

enthalpy of the gas–vapour mixture at this point is calculated as

$$i_g = C_s t_g + \lambda_0 H_g = (2\cdot55)(97\cdot9) + (595)(5\cdot10)$$
$$= 3285 \text{ kcal/kg of dry air}$$

Assuming the mixture at the outlet is saturated at 69·8 °C,

$$H_g = 0\cdot27 \qquad \text{kg/kg of dry air}$$
$$C_S = 0\cdot361 \qquad \text{kcal/kg of dry air °C}$$
$$i_g = 187 \qquad \text{kcal/kg of dry air}$$

The temperatures of the cooling water are (see Table 1),

at the gas inlet $t_l = 14\cdot8$ °C

at the gas outlet $t_l = 8\cdot5$ °C

Thus the operating line can be plotted on the enthalpy–temperature chart as shown in Fig. 2.

Assuming $h_g/k_g' = C_s$, the slope of the tie line is calculated from equation (22′).

At the gas inlet

$$- \beta h_0 C_B/h_B = - (1\cdot436)(2210)(0\cdot0200) =$$
$$- 63\cdot5,$$

At the gas outlet

$$- \beta h_0 C_B/h_B = - (1\cdot049)(2210)(0\cdot0200) =$$
$$- 46\cdot4$$

From points A and Z on the operating line tie lines with these slopes are constructed and the intersections A''' and Z''' give the interface temperatures,

$$t_{iA'''} = 64\cdot2 \text{ °C}$$
$$t_{iZ'''} = 12\cdot4 \text{ °C}$$

Hence, $p_{iA'''} = 181$ mm Hg,
$p_{iZ'''} = 108$ mm Hg.

Since at the gas inlet $p_{gA} = 677$ mm Hg, and at the gas outlet $p_{gZ} = 232$ mm Hg, then

$$(p_{BM})_A =$$
$$\frac{(760 - 181) - (760 - 677)}{2\cdot303 \log (760 - 181)/(760 - 677)} = 255 \text{ mm Hg}$$

$$\left(\frac{p_{BM}}{P - p_i} \right)_A = \frac{255}{579} = 0\cdot441.$$

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Similarly

$$(p_{BM})_Z = 631 \text{ mm Hg}$$

$$\left(\frac{p_{BM}}{P - p_i}\right)_Z = 0.843.$$

The Schmidt numbers are 0·61 at the gas inlet and 0·62 at the gas outlet, and the Prandtl numbers are 0·95 at the gas inlet and 0·79 at the gas outlet.

From equation (5)

$$\alpha_A = (0.441)\left(\frac{0.61}{0.95}\right)^{\frac{1}{2}} = 0.35$$

$$\alpha_Z = (0.843)\left(\frac{0.62}{0.79}\right)^{\frac{1}{2}} = 0.75$$

Hence $\alpha = \dfrac{(0.35 + 0.75)}{2} = 0.55$

The relation between $(i_g - i_g')$ and t at various values of H_g is computed by equation (23) using $\alpha = 0.55$ and plotted in Fig. 2. The saturation curve for i' is also constructed.
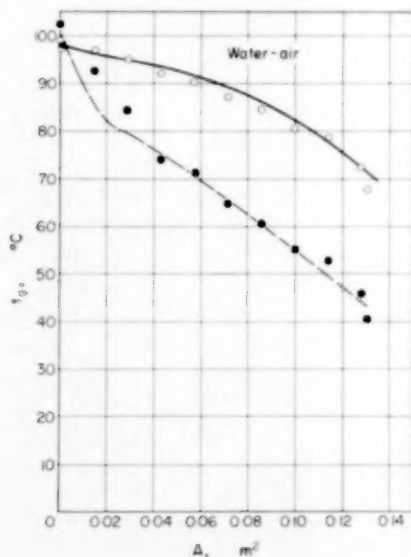
The slope of the tie line is given by equation (22′) as

$$-\alpha \beta h_0 C_B / h_B = -(0.55)(2210)(0.0200)\beta$$
$$= -24.3 \beta$$

At point A of Fig. 2

$$H_g = 5.10, \quad \beta = 1.436, \quad i_g = 3285,$$

and $i_g' = 3170$ is obtained from Fig. 2.

Hence $-\alpha \beta h_0 C_B / h_B = -(24.3)(1.436) =$
$$-34.8$$

A straight line from point a $(i_g' = 3170,$ $t_l = 14.8 \,^{\circ}\text{C})$ with a slope of -34.8 gives the interface conditions at the gas inlet, i.e. $i_i' = 645$ and $t_i = 87.2 \,^{\circ}\text{C}$.

The slope of the path line is obtained from equation (10′)

$$\frac{di_g}{dt_g} = \frac{1}{0.55} \frac{3170 - 645}{97.9 - 87.2} = 430$$

The intersection of the straight line from the

Fig. 3. Comparison of the results of calculation and experiment for the gas temperature change.

Water–Air

—— Run No. 1.	Calculation by the method of
- - - Run No. 3	this paper
○ Run No. 1	
● Run No. 3	Experimental data.

Fig. 4. Comparison of the results of calculation and experiment for the gas temperature change.

Benzene–Air

—— Run No. 12	Calculation by the method of
- - - Run No. 13	this paper.
○ Run No. 12	
● Run No. 13	Experimental data

point A' ($i_g = 3285$, $t_g = 97.9$) with a slope of 430 and the line of constant temperature 92 °C gives a point B' ($i_g = 1183$, $t_g = 92.0$).

These steps are repeated for the remaining points. The results of point to point calculation are shown in Table 3(a). The value of the integration in equation (21') is 3·79. The surface area is therefore

$$A = (0.55)(0.0200)(3.22)(3.79) = 0.134 \text{ m}^2$$

Since the surface area can also be calculated by

$$A = \frac{L \, C_l}{h_0} \int_{t_{l_2}}^{t_{l_1}} \frac{dt_l}{t_i - t_l} \qquad (21'')$$

$$A = \frac{(1445)(1.0)}{2210}(0.194) = 0.127 \text{ m}^2$$

equation (21'') may be simpler to use than equation (21').

Comparison of the calculated results with the value of 0·130 m² used in the experiment indicates that the agreement is good.

The same method of calculation was applied to every run of the four systems, i.e. water–air, benzene–air, toluene–air and methanol–air, the results being tabulated in Table 2. The results of the calculation coincide well with the experimental data. The change in the measured gas temperature in the condenser is compared with the results of calculation in Figs. 3–6. Again there is good agreement between the results of calculation and the experiments.

DISCUSSION

The comparison of the calculation results of the method described above for the water–air system (Run No. 1) with those of COLBURN and HOUGEN [1] and HULDÉN [6] is shown in Table 3(a). The surface areas obtained by these three methods were 0·134 m², 0·136 m² and 0·128 m² respectively, and these results showed good agreement with each other. The results of calculation for the benzene–air system (Run No. 11) are also tabulated in Table 3(b). The agreement is also good.
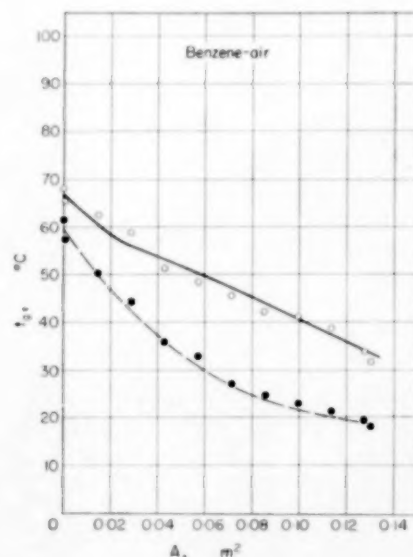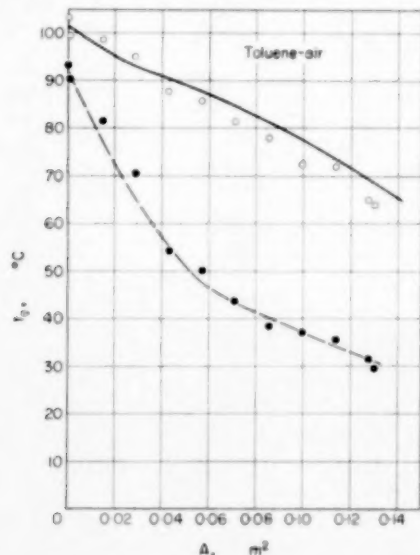

FIG. 5. Comparison of the results of calculation and experiment for the gas temperature change.

Toluene–Air
—— Run No. 21 } Calculation by the method of
--- Run No. 23 } this paper.
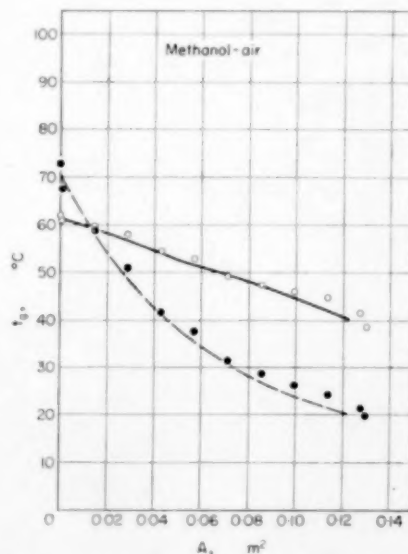o Run No. 21 } Experimental data.
● Run No. 23 }

FIG. 6. Comparison of the results of calculation and experiment for the gas temperature change.

Methanol–Air
—— Run No. 31 } Calculation by the method of
--- Run No. 33 } this paper.
o Run No. 31 } Experimental data.
● Run No. 33 }

Table 2. Summary of calculations

System	Run No.	H_g (kg/kg) inlet	outlet	t_g (°C) inlet	outlet	$(Sc/Pr)_l$ inlet	outlet	$\dfrac{p_{BM}}{P - p_i}$ inlet	outlet	x	h_θ $\left(\dfrac{kcal}{m^2 hr\,°C}\right)$	h_g (inlet) $\left(\dfrac{kcal}{m^2 hr\,°C}\right)$	C_B/h_B	A (m²)	Error (%)
Water–air	1	5·10	0·27	97·9	69·8	0·795	0·885	0·440	0·843	0·55	2210	80	0·0200	0·134	+ 2·9
	2	1·72	0·10	99·9	52·1	0·821	0·907	0·561	0·925	0·65	2740	46	0·0182	0·132	+ 1·5
	3	0·91	0·06	100·2	43·0	0·842	0·915	0·666	0·954	0·72	3060	32	0·0180	0·130	0
	4	0·42	0·03	98·2	32·6	0·873	0·919	0·786	0·979	0·79	3490	24	0·0170	0·126	− 2·9
Benzene–air	11	5·61	1·04	77·2	43·6	0·727	1·040	0·706	0·888	0·72	680	74	0·0178	0·135	+ 3·9
	12	2·97	0·60	66·8	33·2	0·815	1·171	0·760	0·935	0·86	770	48	0·0177	0·134	+ 2·9
	13	0·70	0·28	50·5	18·9	1·122	1·333	0·929	0·984	1·18	1250	24	0·0167	0·128	− 1·5
Toluene–air	21	6·22	0·89	101·1	64·8	0·599	0·996	0·652	0·900	0·64	680	96	0·0205	0·141	+ 8·3
	22	2·29	0·37	97·8	46·4	0·748	1·223	0·787	0·957	0·88	910	49	0·0198	0·147	+ 13·1
	23	0·63	0·17	91·8	30·7	1·060	1·412	0·925	0·983	1·19	1340	26	0·0180	0·132	− 1·5
Methanol–air	31	2·92	0·56	61·5	40·0	0·805	0·977	0·674	0·864	0·69	1060	55	0·0194	0·122	− 6·2
	32	1·39	0·29	62·9	30·3	0·870	1·047	0·745	0·935	0·81	1230	36	0·0186	0·122	− 6·2
	33	0·29	0·13	70·3	20·4	1·039	1·102	0·924	0·983	1·02	2100	20	0·0168	0·122	− 6·2

Table 3. Factors determined from three calculation methods

(a) *Water–air.*   *Run No. 1.*

Method of this paper $A = 0.134\ \text{m}^2$.   Error $= +\ 3.1$ per cent

Point No.	t_g (°C)	p_v (mm Hg)	H_g (kg/kg)	i_g (kcal/kg)	i'_g (kcal/kg)	i'_i (kcal/kg)	$i'_g - i'_i$ (kcal/kg)	t_i (°C)	t_l (°C)	β	$\dfrac{z\beta h_0 C_B}{h_B}$	$\dfrac{10^3 \beta}{i'_g - i'_i}$
1	97.9	677	5.10	3285	3170	645	2525	87.2	14.8	1.436	34.8	0.57
2	92.0	567	1.83	1183	1141	50	1091	46.3	10.5	1.231	29.9	1.13
3	87.0	469	1.00	656	631	23	608	31.2	9.4	1.149	27.9	1.89
4	82.0	385	0.64	422	405	14	391	23.6	9.0	1.104	26.8	2.82
5	77.0	314	0.44	294	279	10	269	19.0	8.8	1.076	26.1	4.00
6	72.0	255	0.32	215	204	9	195	16.2	8.6	1.056	23.6	5.42
7	69.8	232	0.27	187	178	8	170	15.2	8.5	1.049	23.5	6.17

COLBURN and HOUGEN's method $A = 0.136\ \text{m}^2$.   Error $= +\ 4.6$ per cent

Point No.	t_g (°C)	p_v (mm Hg)	H_g (kg/kg)	h_g $\left(\dfrac{\text{kcal}}{\text{m}^2\text{hr °C}}\right)$	Pr	Sc	$k_g p_{BM}$	λ_c (kcal/kg)	t_i (°C)	p_i (mm Hg)	t_l (°C)	$t_i - t_l$ (°C)	$\dfrac{10^5}{h_0(t_i - t_l)}$	Q (kcal/hr)
1	97.9	677	5.10	89	0.95	0.61	13.83	541	88.1	489	14.8	73.3	0.62	9975
2	92.0	567	1.83	46	0.90	0.61	7.02	544	50.0	93	10.5	39.5	1.15	3215
3	87.0	469	1.00	33	0.88	0.63	5.02	547	30.8	33	9.5	21.3	2.12	1508
4	82.0	385	0.64	26	0.85	0.63	4.08	550	22.2	20	9.0	13.2	3.43	757
5	77.0	314	0.44	22	0.88	0.63	3.59	553	17.7	15	8.7	9.0	5.04	345
6	72.0	255	0.32	21	0.80	0.62	3.21	556	14.8	13	8.6	6.2	7.26	90
7	69.8	232	0.27	20	0.79	0.62	3.09	557	14.0	12	8.5	5.5	8.25	0

HOLDÉN's method $A = 0.128\ \text{m}^2$.   Error $= -\ 1.5$ per cent

Point No.	t_g (°C)	p_v (mm Hg)	F	θ	h_g $\left(\dfrac{\text{kcal}}{\text{m}^2\text{hr °C}}\right)$	h_0/h_g	t_i (°C)	t_l (°C)	$t_i - t_l$ (°C)	$\dfrac{10^5}{h_0(t_i - t_l)}$	Q (kcal/hr)
1	97.9	677	1628	3688	89	24.7	88.8	14.8	74.0	0.61	9975
2	92.0	567	1628	2319	46	48.5	54.2	10.6	43.6	1.04	3215
3	87.0	469	1628	1647	33	67.2	32.1	9.2	22.9	1.97	1508
4	82.0	385	1628	1230	27	82.5	23.2	9.0	14.2	3.19	757
5	77.0	314	1628	943	23	94.8	18.2	8.8	9.4	4.78	345
6	72.0	255	1628	734	21	105.3	15.2	8.6	6.6	6.82	90
7	69.8	232	1628	660	20	108.8	14.2	8.5	5.7	7.96	0

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Table 3. Factors determined from three calculation methods

(b) Benzene-air. Run No. 11

Method of this paper $A = 0.135 \text{ m}^2$. Error $= \pm 3.9$ per cent

Point No.	t_g (°C)	H_g (kg/kg)	i_g (kcal/kg)	i_g' (kcal/kg)	i_i' (kcal/kg)	$i_g' - i_i'$ (kcal/kg)	t_l (°C)	t_i (°C)	β	$\dfrac{z\beta h_0 C_B}{h_B}$	$\dfrac{10^3 \beta}{i_g' - i_i'}$
1	77·2	5·61	789	701	216	485	11·8	52·8	1·458	11·8	3·01
2	71·0	4·35	567	539	147	392	11·4	46·1	1·398	11·3	3·57
3	65·0	3·36	435	415	104	311	11·1	39·7	1·342	10·9	4·31
4	59·0	2·58	333	318	77	241	10·9	34·1	1·291	10·4	5·35
5	53·0	1·77	229	219	54	165	10·6	27·3	1·226	9·9	7·42
6	47·0	1·25	163	156	42	114	10·5	22·5	1·176	9·5	10·31
7	43·6	1·04	134	128	37	91	10·4	20·1	1·153	9·3	12·61

Colburn and Hougen's method $A = 0.144 \text{ m}^2$. Error $= \pm 10.8$ per cent

Point No.	t_g (°C)	p_v (mm Hg)	H_g (kg/kg)	Pr	Sc	h_g $\left(\dfrac{\text{kcal}}{\text{m}^2\text{hr}°\text{C}}\right)$	$k_g p_{BM}$	λ_v (kcal/kg)	t_i (°C)	t_l (°C)	p_i (mm Hg)	$t_i - t_l$ (°C)	$\dfrac{10^5}{h_0(t_i - t_l)}$	Q (kcal/hr)
1	77·2	513	5·61	0·73	0·39	74	5·63	94·9	53·9	11·8	313	42·1	3·76	2050
2	71·0	439	4·11	0·73	0·43	59	4·61	96·0	45·3	11·4	226	34·0	4·67	1356
3	65·0	406	3·10	0·72	0·47	49	3·95	97·2	37·8	11·1	168	26·7	5·92	911
4	59·0	357	2·38	0·74	0·54	41	3·40	98·2	31·3	10·9	127	20·5	7·73	588
5	53·0	303	1·77	0·74	0·62	35	2·93	99·2	25·6	10·6	98	15·0	10·60	323
6	47·0	242	1·25	0·74	0·73	29	2·50	100·1	20·4	10·5	76	9·9	15·98	98
7	43·6	211	1·04	0·74	0·80	27	2·34	100·6	18·2	10·4	69	7·8	20·40	0

Hougen's method $A = 0.126 \text{ m}^2$. Error $= \pm 3.1$ per cent

Point No.	t_g (°C)	p_v (mm Hg)	F	θ	h_g $\left(\dfrac{\text{kcal}}{\text{m}^2\text{hr}°\text{C}}\right)$	h_0/h_g	t_i (°C)	t_l (°C)	$t_i - t_l$ (°C)	$\dfrac{10^5}{h_0(t_i - t_l)}$	Q (kcal/hr)
1	77·2	513	653	811	74	8·5	55·8	11·8	44·0	3·60	2050
2	71·0	465	653	687	64	9·8	48·8	11·4	37·4	4·23	1430
3	65·0	412	653	576	57	11·2	41·5	11·1	30·4	5·20	967
4	59·0	356	653	476	50	12·5	34·8	10·8	24·0	6·62	612
5	53·0	303	653	385	46	13·9	28·7	10·7	18·0	8·77	334
6	47·0	242	653	297	41	15·4	23·1	10·5	12·6	12·58	100
7	43·6	211	653	255	39	16·1	20·6	10·4	10·2	15·60	0

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In the calculation of h_0 the vapour film coefficient is obtained from Nusselt's equation. For the water–air system where the vapour film coefficient is very high an average value of the coefficient throughout the condenser may be used. However, for systems other than water–air, where the value of the vapour film coefficient is relatively small, the point value should be taken. For the methanol–air system (Run No. 31) the value of h_0 varied from 6600 at the gas inlet to 800 at the gas outlet, and the surface area obtained from the calculation using the point value of the vapour film coefficient was 0·121 m². The surface area obtained from the calculation with a constant average value $h_0 = 1060$ was 0·122 m², the two results for the surface area being nearly equal. Therefore, as shown in Table 2, the values for h_0 were taken as constant throughout the condenser for all systems.

If the amount of heat to be transferred is calculated from the enthalpy change of the gas, it includes the heat necessary to cool the condensate to 0 °C. Actually, the temperature of the condensate lies between t_g and t_i. From this point of view, the graphical method using the enthalpy chart of the gas gives a conservative estimate of the heat transfer surface area.

NOTATION

A	area of transfer surface	m²
C	specific heat	kcal/kg °C
C_S	humid heat	kcal/kg of dry gas °C
F	factor defined in reference [6]	
G_B	flow rate of stagnant gas	kg of dry gas/hr
G'	mass velocity of gas vapour mixture	kg/m² hr
H	humidity	kg/kg of dry gas
h	coefficient of heat transfer	kcal/m² hr °C
h_B	fictitious coefficient of heat transfer when only stagnant gas flows	kcal/m² hr °C
k_0	combined conductance other than the gas film	kcal/m² hr °C
i	enthalpy of gas vapour mixture	kcal/kg of dry gas
i'	modified enthalpy of gas vapour mixture	kcal/kg of dry gas
j	j factor in heat transfer	
k_g'	mass transfer coefficient	kg/m² hr (kg/kg of dry gas)
k_g	mass transfer coefficient	kg/m² hr mm Hg
L	flow rate of cooling water	kg/hr
P	total pressure in condenser	mm Hg
p	partial vapour pressure	mm Hg
P_{BM}	average partial pressure of stagnant gas in gas film	mm Hg
t	temperature	°C
α	constant defined by equation (4)	
β	variable defined by equation (20)	
λ_0	latent heat of vapourization at 0° C	kcal/kg
θ	hypothetical temperature defined in reference [6]	
Pr	Prandtl number	
Re	Reynolds number	
Sc	Schmidt number	

Subscripts

B	stagnant gas
g	gas–vapour mixture or gas film
i	interface
l	cooling water

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Studies in optimization—II

Optimum temperature gradients in tubular reactors

R. Aris

Department of Chemical Engineering, University of Minnesota, Minneapolis 14, Minnesota.

Abstract—The method of dynamic programming is used to solve the general problem of finding the temperature gradient in a tubular reactor, which will maximize some function expressing the profit made by the reaction. As an introductory example the reaction $A \rightarrow B \rightarrow C$ when the yield of B is to be maximized is considered. This is followed by a detailed analysis of this reaction for first order kinetics, which confirms and extends the work of Amundson and Bilous. The solution of the general problem for a number of simultaneous reactions is then presented and some extensions discussed.

Résumé—La méthode de programmation dynamique est utilisée pour résoudre le problème général de la détermination du gradient de température dans un réacteur tubulaire, qui portera au maximum la fonction exprimant le progrès d'une réaction. L'exemple préliminaire est celui de la réaction $A \rightarrow B \rightarrow C$ quand le rendement de B est poussé au maximum. Suit une analyse détaillée de cette réaction pour une cinétique d'ordre 1 qui confirme et étend le travail d'Amundson Bilous. La solution du problème général pour un certain nombre de réactions simultanées est ensuite présenté et son extension discutée.

Zusammenfassung—Die Methode der dynamischen Programmierung wird benutzt, um das allgemeine Problem zu lösen, den Temperaturgradienten in einem Rohrreaktor zu finden, bei dem eine Funktion den Reaktionsfortschritt ausdrückt, die den Maximalwert annimmt. Als einführendes Beispiel wird die Reaktion $A \rightarrow B \rightarrow C$ betrachtet, bei der die Ausbeute von B ein Maximum erreichen soll. Es folgt eine ins Einzelne gehende Analyse dieser Reaktion unter der Voraussetzung, dass die Teilschritte nach der ersten Ordnung verlaufen. Damit wird die Arbeit von Amundson und Bilous bestätigt und erweitert. Im Anschluss daran wird die Lösung des allgemeinen Problems für eine Reihe von Simultanreaktionen angegeben, und einige Erweiterungen werden diskutiert.

1. Introduction

It has long been known that for a single reaction taking place in a tubular reactor the best yield is obtained if the temperature is so adjusted as to make the reaction rate as large as possible at each point of the reactor [1, 2, 3, 4]. In the case of two or more competing reactions this no longer true, as Amundson has shown [5]. The problem of two consecutive reactions $A \rightarrow B \rightarrow C$ has been extensively discussed in the work of Bilous and Amundson [4] and they derive an equation to be solved simultaneously with reaction equations to give the optimum temperature profile. They use two methods, the first based on an explicit solution of the reaction equations, and the second an implicit method which may be applied to the reaction equations themselves. Both involve the rather difficult notions of functional differentiation [6] and, perhaps because of this, their work has not received the attention it deserves.

In the present paper we wish to show that these problems may be solved by the methods of dynamic programming. These have been developed in quite other fields of study but the new formalism of the calculus of variations given by Bellman is extraordinarily apt for just such problems as we are concerned with. Bellman ([7] Chap. IX) discusses the maximization of an integral

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$$J(z) = \int_0^T F(x_1, x_2, \ldots x_n; z)\, dt \qquad (1)$$

where the function $z(t)$, $0 \leqslant t \leqslant T$, has to be chosen to give the maximum value of J and the x_i are determined by the differential equations

$$\frac{dx_i}{dt} = G_i(x_1, \ldots x_n, z), \quad x_i(0) = c_i, \qquad (2)$$
$$i = 1, 2, \cdots n$$

and subject to quite general restrictions

$$R_k(x_1, \ldots x_n, z) \leqslant 0. \qquad (3)$$

Now if we think of the x_i as concentrations or partial pressures, z as the temperature, and t as the current holding time along the reactor whose total holding time is T, his formulation is just what we need. For if, for example, we wish to maximize the yield of the first component, putting $F = G_1$ gives $J = x_1(T) - x_1(0)$, the increase in its concentration. The equations (2) are the equations for the rates of reaction and the conditions (3) include such restrictions as insisting that the concentrations be positive and bounded ($0 \leqslant x_i \leqslant x_i^*$) or that the temperature be within certain limits ($z_* \leqslant z \leqslant z^*$). We shall apply BELLMAN's methods to the general problem and give a detailed treatment of the case $A \to B \to C$ which AMUNDSON and BILOUS studied, incidentally resolving two questions that they left open.

2. THE DYNAMIC PROGRAMME FOR A CONTINUOUS DECISION

The determination of the optimum temperature gradient may be regarded as making a continuous decision. At each point the temperature has to be chosen so as to maximize the eventual yield of the process. This choice will depend on the concentrations at the point and on the holding time of the remainder of the process, and is called the optimum policy relative to this state and holding time. Now whatever policy may have been adopted up to a given point the overall optimum cannot possibly be attained unless the part of the reactor beyond this point uses the optimum policy with respect to the state at that point and the remaining holding time. In fact if we vary the policy in the first section and always use the optimum policy in the second section the maximum over all such variations will give the optimum for the whole. But in this case we have only to vary the temperature in the first section, which can be as short as we please. This suggests a way of building up the solution and we will illustrate it by a definite example. Suffice it to say that the basis of the method has been enshrined by BELLMAN in the so-called principle of optimality, that " an optimal policy has the property that whatever the initial state and initial decision are, the remaining decisions must constitute an optimal policy with regard to the state resulting from the first decision." ([7], p. 83). This simple statement is worth weighing; its proof is immediate but it is pregnant with the most diverse applications.

Consider the consecutive reactions $A \to B \to C$ with C a waste product and B the product of value; as BILOUS and AMUNDSON remark ([2] p. 88) several reactions may be included under this form. If x and y are the concentrations of A and B the kinetics of the reactions are given by

$$\frac{dx}{dt} = -a(T)\, F(x) \qquad (4)$$

$$\frac{dy}{dt} = na(T)\, F(x) - b(T)\, G(y) \qquad (5)$$

where t is the holding time of the reactor up to a given point and $T(t)$ the temperature there. $a(T)$ and $b(T)$ are the rate constants of the reactions. The yield of B over the total holding time $t = S$ of the reactor has to be maximized, and this is

$$y(S) - y(0) = \int_0^S \frac{dy}{dt}\, dt =$$
$$= \int_0^S \{n\, a(T)\, F(x) - b(T)\, G(y)\}\, dt \qquad (6)$$

When the optimum temperature policy $T(t)$, $0 \leqslant t \leqslant S$, has been found the resulting maximum will be a function of x_0, y_0, and S. Let

$$f(x_0, y_0, S) =$$
$$\text{Max} \int_0^S \{ n\,a\,(T)\,F\,(x) - b\,(T)\,G\,(y) \} dt \quad (7)$$

then dividing the total holding time interval (O, S) into a very short first section (O, s) and the remainder (s, S) and applying the principle of optimality

$$f(x_0, y_0, S) =$$
$$\text{Max} \left[\int_0^S (naF - bG) dt + f(x(s), y(s), S - s) \right], \quad (6)$$

where in this maximization we have only to choose $T(t)$ over the interval (O, s). Now let s be very small then

$$f(x_0, y_0, S) = \text{Max} \left[(naF - bG)_0\, s + f(x_0, y_0, S) \right.$$
$$\left. + \left\{ \frac{\partial f}{\partial x_0} \left(\frac{dx}{dt} \right)_0 + \frac{\partial f}{\partial y_0} \left(\frac{dy}{dt} \right)_0 - \frac{\partial f}{\partial S} \right\} s + 0\,(s^2) \right]$$

where a suffix 0 denotes values at the inlet $t = 0$ and the maximization is now over the choice of $T(s)$ at $s = 0$, i.e. T_0. In this equation second and fifth terms on the right side are unaffected by the maximization and the second is equal to the left side. Thus using (4) and (5) the equation can be rearranged and letting $s \to 0$ we have

$$\frac{\partial f}{\partial S} = \text{Max}_{T_0} \left\{ (naF - bG)_0 \left(1 + \frac{\partial f}{\partial y_0} \right) - \right.$$
$$\left. - (aF)_0 \frac{\partial f}{\partial x_0} \right\} \quad (9)$$

This maximum must be sought subject to the physical restriction $T_* \leqslant T_0 \leqslant T^*$, where T_* and T^* are the minimum and maximum permitted temperatures. It is a valuable feature of dynamic programming that it is not at all embrassed by such restrictions; conventional calculus of variations is more bashful.

If the value of T_0 is free of restrictions the optimum value may be found by differentiating equation (9). Thus T_0 should satisfy

$$0 = \{ n\,a'\,(T_0)\,F\,(x_0) - b'\,(T_0)\,G\,(y_0) \}$$
$$\left(1 + \frac{\partial f}{\partial y_0} \right) - a'\,(T_0)\,F\,(x_0) \frac{\partial f}{\partial x_0} \quad (10)$$

and a partial differential equation of the first order for f would result from eliminating T_0 between equation (10) and

$$\frac{\partial f}{\partial S} = \{ na\,(T_0)\,F\,(x_0) - b\,(T_0)\,G\,(y_0) \}$$
$$\left(1 + \frac{\partial f}{\partial y_0} \right) - a\,(T_0)\,F\,(x_0) \frac{\partial f}{\partial x_0} \quad (11)$$

Since rate constants such as a or b are generally monotonic functions of temperature it is possible and advantageous to take one of them as the independent variable. Let $b = b\,(a)$ and $db/da = b'\,(T)/a'\,(T) = A\,(a)$, thus a has to be eliminated between

$$f_S = (naF - b\,(a)\,G)(1 + f_y) - aFf_x \quad (12)$$

and $0 = (nF - A\,(a)\,G)(1 + f_y) - Ff_x \quad (13)$

(Here the notation $f_S = \partial f/\partial S$, $f_x = \partial f/\partial x_0$. $f_y = \partial f/\partial y_0$ is used for simplicity).

Suppose that the equation obtained by eliminating a between (12) and (13) is

$$H\,(f_x, f_y, f_S, x_0, y_0) = 0 \quad (14)$$

for clearly f itself and S do not occur. The characteristic equations of this partial differential equation are

$$\frac{dx_0}{d\tau} = \frac{\partial H}{\partial f_x}, \quad \frac{dy_0}{d\tau} = \frac{\partial H}{\partial f_y}, \quad \frac{dS}{d\tau} = \frac{\partial H}{\partial f_S} \quad (15)$$

$$\frac{df_x}{d\tau} = -\frac{\partial H}{\partial x_0}, \quad \frac{df_y}{d\tau} = -\frac{\partial H}{\partial y_0}, \quad \frac{df_S}{d\tau} = 0 \quad (16)$$

where τ is a parameter along the characteristic. It may be well to notice the importance of the last equation of (16) at this point. f_S is the partial derivative of the optimum profit with respect to reactor length S, and the equation shows that this does not change along a characteristic. Naturally we are only interested in the region in which $f_S > 0$ for if $f_S < 0$ it is unprofitable to continue the reaction.

If the elimination of a between (12) and (13) is explicitly possible we arrive at an expression for H and thence to the characteristic equations (15) and (16). However, even if this is not possible the characteristic equations can be found from the two equations by differentiating them partially with respect to f_x, f_y etc. and eliminating the partial derivatives of a. This gives

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$$\frac{dx_0}{d\tau} = -aF \qquad (17)$$

$$\frac{dy_0}{d\tau} = naF - bG \qquad (18)$$

$$\frac{dS}{d\tau} = -1 \qquad (19)$$

$$\frac{df_x}{d\tau} = aF'\{f_x - n(1 + f_y)\} \qquad (20)$$

$$\frac{df_y}{d\tau} = bG'(1 + f_y) \qquad (21)$$

These equations are not complete in themselves unless (13) can be solved for a and a substituted in them, but in this case the elimination would be explicitly possible. However, we can find an equation for a along the characteristic by differentiating (13) with respect to τ and substituting from (17–21). This gives

$$\frac{da}{d\tau} = -aB(a)\frac{F(x_0) G'(y_0)}{G(y)_0} \qquad (22)$$

where

$$B(a) = \{b(a) - aA(a)\}/A'(a). \qquad (23)$$

It is at first sight rather remarkable that f_x and f_y do not appear in equation (22), for it now allows the four equations (17)–(19), (22) to be solved simultaneously. We shall show later that this always comes about with two simultaneous reactions but is not to be expected with more than two.

It is interesting to compare these four equations with those of AMUNDSON and BILOUS [2]; (17) and (18) compare with their (25) and (26) and show that the characteristics of our partial differential equation are reaction paths; (22) divided by da/dT gives their equation (32). The important difference between our equation and theirs is that the sign of $dS/d\tau$ is negative. This is because we are integrating from the end of the reactor not from the beginning and carries with it the advantage that we can determine the initial value of a instead of finding it by trial and error. To do this we observe that when $S = 0$, $f(x_0, y_0, 0) = 0$ and hence f_x and f_y are zero everywhere on this manifold. It follows from (13) that the initial value of a is given by

$$A(a) = nF(x_0)/G(y_0) \qquad (24)$$

But this is just the so-called zero function which AMUNDSON and BILOUS use to tell them where to stop the integration. Equation (12) immediately shows what points are worth considering as starting points for

$$f_S = naF(x_0) - b(a)G(y_0) \qquad (25)$$

when $S = 0$ and a is given by (24); we are only interested in regions of the x_0, y_0 plane that make f_S positive.

Up to this point we have merely confirmed AMUNDSON and BILOUS' analysis by an entirely different method, but this has no great advantage unless it be that the theory of first order partial differential equations is better known than that of functionals. We have still a need for trial and error for, whilst they had no means of knowing what the initial temperature should be, we have no idea of what the values of x_0 and y_0 may be at the end of the integration. However in the matter of restrictions the method of dynamic programming has a distinct advantage over functional analysis for with the latter it would be very hard to say what should be done with such an inequality as $T_* \leqslant T \leqslant T^*$. Moreover it is essential to impose a restriction of this kind, for if $G(y_0) = 0$, the optimum temperature required by (13) becomes infinite; such is the case with a feed of pure A.

Since $a(T)$ is a monotonic function of T the restriction on T implies a similar restriction on a.

$$a^* \leqslant a \leqslant a^*. \qquad (26)$$

As soon as the value of a demanded by equation (13) goes outside these limits a must be fixed at that limit and equation (12) is then integrated with constant a (equal to a_* or a^*). The characteristic equations for this are again (17)–(21), but here a is fixed at a_* or a^* and the equations are easily integrable. In the initial manifold $S = 0$ where a is given as a function of $x_0 y_0$ and by (24) we can define two curves Γ_* and Γ^* along which the value a is a_* or a^*. Between these curves the initial value of f_s is given by eliminating a between (24) and (25). Outside these curves f_S will still be given by (25) but with a

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fixed at a_* or a^*. Two other curves Δ_* and Δ^* can be drawn along which $f_s = 0$ for $a = a_*$ and a^* respectively. If $(b/a - db/da)$ does not change sign (and this is usually the case) one of the curves will lie between the two Γ curves. This is illustrated in Fig. 1 where Δ^* lies between Γ_* and Γ^* and in this case f_S is positive in the whole area between Δ^* and the axis $y_0 = 0$. Thus the region of initial points of interest is between Δ_* and the x_0 axis.
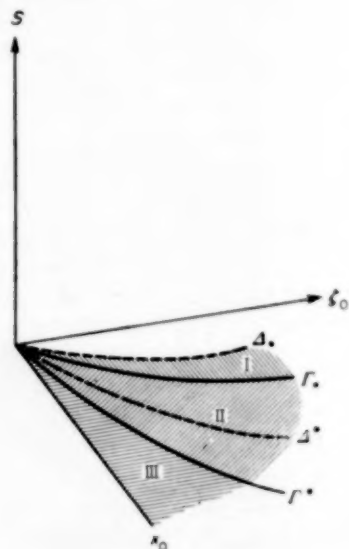
Fig. 1. The regions of interest on the initial manifold.

We can now describe the way in which a complete solution of our problem is to be generated. Let the three regions of the initial manifold be denoted by

$$\text{I}: \quad a = a_*, \, f_S > 0$$
$$\text{II}: \quad a_* < a < a^*, \, f_S > 0$$
$$\text{III}: \quad a = a^*, \, f_S > 0.$$

Consider first a point $x_0 = \xi$, $y_0 = \eta$ in the region II. The initial values for the integration of the characteristic equations (17)–(22) are $x_0 = \xi$, $y_0 = \eta$, $S = f_x = f_y = 0$ and a is given by $A(a) = nF(\xi)/G(\eta)$. These six equations are to be integrated until either $a = a^*$ or x_0 or $y_0 = 0$. In case $a = a^*$ we continue to integrate

the equations (17)–(21) but with a kept constant until x_0 or $y_0 = 0$. If (ξ, η) be in the region I we must integrate the equations with $a = a^*$ constant but substitute the values of x_0, y_0, f_x and f_y into equation (13) until $a = a^*$, or until x_0 or $y_0 = 0$ whichever may happen first. In the latter case the complete trajectory has been found, but in the former case we must continue the integration of the full characteristic equations (17)–(22) until either $a = a^*$ or x_0 or $y_0 = 0$, and if a reaches a^* switch again to the equations with constant $a = a^*$. Similarly from region III the equations with constant $a = a^*$ are integrated but with an eye on equation (13) lest the unconstrained maximum should fall below a^*. This however is unlikely for $B(a)$ does not normally change sign. Thus a whole region of x_0, y_0, S space is swept out and for each point of this region the value of $f(x_0, y_0, S)$ and the appropriate inlet temperature $a(x_0, y_0, S)$ is known. If we are given the holding time S and the inlet concentrations x_0, y_0 of A and B we find the maximum yield immediately as $f(x_0, y_0, S)$. The temperature policy is given by the values of a along the characteristic from the point x_0, y_0, S to the plane $S = 0$. For by (17) and (18) the characteristic is a reaction path and the value of a at a distance s along it is the optimum inlet value of a to a reactor of length $S - s$ when the concentrations are $x(s)$, $y(s)$ and by the principle of optimality this is just the optimum temperature at this point.

3. Consecutive First Order Reactions

The foregoing example has been discussed in some detail as being sufficiently simple to introduce the method yet general enough to be interesting. We will now give some definite results on the case that Amundson and Bilous discussed before treating more general problems. In doing so we can exhibit a device that is often useful in reducing the number of variables and dispose of two questions which the earlier work left unresolved. The results of the last paragraph would be two functions $f(x_0, y_0, S)$ and $a_0(x_0, y_0, S)$ the optimum yield and initial temperature of a reactor of holding time S and with inlet concentrations x_0 and y_0, and such

functions can be represented as contour surfaces in [3] space. This, however, is not convenient and it would be of value to work with functions of only two variables. In the case of first order reactions $F(x) = x$, $G(y) = y$ this is possible for the equations are homogeneous in the concentrations and we can take $z = y/x$, their ratio as the dependent variable.

Letting $n = 1$, $F = x$, $G = y$ in equations (4) and (5) we have

$$\frac{dx}{dt} = -ax \qquad (27)$$

$$\frac{dy}{dt} = ax - by, \qquad (28)$$

whence

$$\frac{dz}{dt} = a + (a - b)z, \qquad (29)$$

with $z = z_0 = y_0/x_0$ when $t = 0$. The maximum yield of B will be proportional to x_0 so we write

$$f(x_0, y_0, S) = x_0 g(z_0, S) \qquad (30)$$

and since $f_S = x_0 g_S$, $f_x = g - z_0 g_z$, $f_y = g_z$ we have in place of (9) the equation

$$g_S = \max_{a_0} \left[(a - bz_0)(1 + g_z) - a(g - z_0 g_z) \right]. \quad (31)$$

A common form of the rate coefficients a and b is $a = k_1 \exp(-E_1/RT)$ and $b = k_2 \exp(-E_2/RT)$ in which case

$$b = \rho a^{1/r} \qquad (32)$$

where $r = E_1/E_2$ and $\rho = k_2 k_1^{-1/r}$

In this case $A(a) = db/da = (\rho/r) a^{(1-r)/r}$ and $B(a) = -ra^2$, and the condition for an unrestricted maximum in equation (31) is

$$a^{(1-r)/r} = \frac{r}{\rho} \frac{1 + (1 + z_0) g_z - g}{x_0 (1 + g_z)} \qquad (33)$$

Substituting this into equation (31) gives the non-linear equation

$$g_S = (1 - r) \left(\frac{r}{\rho} \right)^R \frac{\{ 1 + (1 + z_0) g_z - g \}^{R+1}}{z_0^R (1 + g_z)^R} \qquad (34)$$

where $R = r/(1 - r)$. The characteristic equations are

$$\frac{dz_0}{d\tau} = a \{ 1 + (1 - \rho a^{(1-r)/r} z_0 \}. \qquad (35)$$

$$\frac{dS}{d\tau} = -1, \qquad (36)$$

$$\frac{dg}{d\tau} = a(g - 1) + \rho a^{1/r} z_0 g_z, \qquad (37)$$

$$\frac{dg_z}{d\tau} = \rho a^{1/r} (1 + g_z). \qquad (38)$$

$$\frac{dg_S}{d\tau} = a g_S. \qquad (39)$$

and $\quad \dfrac{da}{d\tau} = \dfrac{ra^2}{z_0}. \qquad (40)$

Formidable though these may seem it is actually possible to find a solution in finite terms, for dividing (35) by (40) we would have a single ordinary differential equation of Riccati's form for z_0 as a function of a. Letting $\beta(a) = (b - a)/ra^2$ the standard method of solution gives

$$z_0 =$$

$$\zeta_0 \frac{\{\exp \beta(a)/a^{1/r} \beta(a)\}}{\{\exp \beta(a_0)/a_0^{1/r} \beta(a_0)\} + \zeta_0 \displaystyle\int_{a_0}^{a} a^{-1/r} \exp \beta(a)\, da} \qquad (41)$$

for the solution for which $z_0 = \zeta_0$ when $a = a_0$. However this answer would require considerable computation for the next step is to substitute in (40) and integrate for time τ as a function of a. The modern digital computer is as well adapted to the solution of a set of simultaneous ordinary differential equations (35)–(40), as it is to the integrations required by (41).

We have to solve (31) subject to the boundary condition $g(z_0, 0) = 0$, that is to find the surface $g(z_0, S)$ that passes through the z_0 axis. To find the initial values that the dependent variables in (35)–(40) must take we observe that this condition implies $g = g_z = S = 0$ and for any $z_0 = \zeta$, g_S and a are given by (34) and (33)

$$(g_s)_0 = (1 - r) a_0 = (1 - r)(r/\rho z_0)^R. \qquad (42)$$

It is now clear that some restraints must be put on a for this would otherwise require it to be infinite when $z_0 = 0$, $R > 0$. Let the inequality restrictions (26) be imposed. Then we can say at once

that only where the formula (33) gives a value of a in the range (a_*, a^*) do the preceeding equations (34)–(40) apply. If the value is outside then the equation (31) has to be solved with a held constant at either its upper or lower bound. This would lead to the same set of characteristic equations (35)–(39) but with $a = a^*$ or $a = a^*$. These however are easily soluble and give

$$g(z_0, S) =$$
$$\frac{\exp(-aS) - \exp(-bS)}{[(b/a) - 1]} - z_0[1 - \exp(-bS)] \quad (43)$$

with a and $b(a)$ at one of these values. Naturally the region of interest is bounded by the curve on which $g_S = 0$ for beyond this point it is not worth reacting. Equation (39) shows that $g_S = 0$ is a characteristic, and since it passes through the point on the z_0 axis at which $g_S = 0$, namely $z_0 = a_*/b(a_*) = a_*/b_*$, it has the equation

$$b_*\{a_* + (a_* - b_*)z_0\} = a_*^2\exp - (a_* - b_*)S. \quad (44)$$

We may now distinguish three distinct cases according as $r = 1$, $0 < r < 1$ and $r > 1$ which we will consider in turn.

$r = 1$.

This case is somewhat special since $E_1 = E_2$ and the relative rates of the two reactions are unchanged by temperature. It follows that if the concentrations favour the production of B then the greatest possible temperature should be used to achieve this as fast as possible. As soon as the concentrations lead to the production of C at the expense of B the reaction should stop. This may be seen analytically from equation (31) with $b = \rho a$ for

$$g_S = a^*\{(1 + g_2 - g) - z_0(\overline{\rho - 1}\, g_2 + \rho)\}$$

whenever it is positive. Then the solution is given by (43) with $a = a^*$, $b = \rho a^*$.

$0 < r < 1$.

In this case we observe that $R = r/(1 - r)$ is positive and ranges from 0 to infinity. It follows that on the initial line, the z_0-axis, there will be three regions:

I. $\quad 0 \leqslant z_0 \leqslant z_* = (r/\rho)(a^*)^{-1/R}$
$\quad\quad$ where $a_0 = a^*$.

II. $\quad z_* \leqslant z_0 \leqslant z^* = (r/\rho)(a_*)^{-1/R}$
$\quad\quad$ where $a_* \leqslant a_0 \leqslant a^*$.

III. $\quad z^* \leqslant z_0 \leqslant Z = (1/\rho)(a_*)^{-1/R}$
$\quad\quad$ where $a_0 = a^*$.

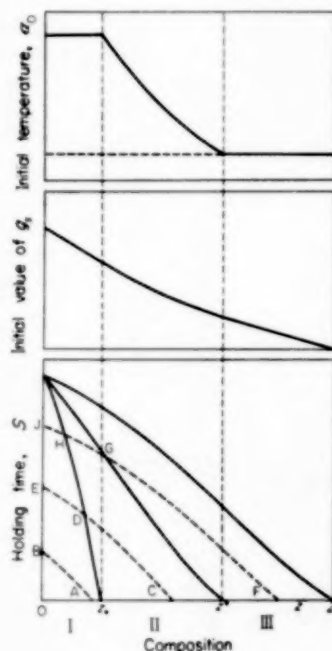$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (45)$

Fig. 2. Integration of the characteristic equations.

These are shown in Fig. 2 in the top section of the figure. The corresponding initial value of g_S is given by either (31) or (42) and is shown in the second section.

I. $\quad (g_S)_0 = a^* - b^* z_0$

II. $\quad (g_S)_0 = (1 - r)(r/\rho\, z_0)^R,$

III. $\quad (g_S)_0 = a_* - b_* z_0.$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (46)$

and it can be shown that $(g_S)_0$ has a continuous derivative with respect to z_0.

The way the integration of the characteristic equations proceeds can be illustrated by considering three typical characteristic paths. In the first, AB, we start from a point A in the region I

where the required temperature a_0 is maximum. The initial value of g_S is given by (46) and the integration of equations (35)–(39) proceeds with $a = a^*$ until z_0 becomes zero (the other possibility of the optimum a falling below a^* does not occur). With a characteristic, such as CDE, emanating from the region II we start in the region where the optimum a is unconstrained and the full set of equations (35)–(40) applies with initial values given by (45) and (46). The integration proceeds until a point D is reached at which $a = a^*$ after which the characteristic equations for constant $a = a^*$ must be used until $z_0 = 0$ at E. When a characteristic starts from the third region, the first part of it FG is found by integrating the equations with $a = a_*$. However a point G will be reached at which the criterion (33) for an unrestricted optimum a demands a value greater than a_*. From this point the full equations must be integrated until H where $a = a^*$ and from
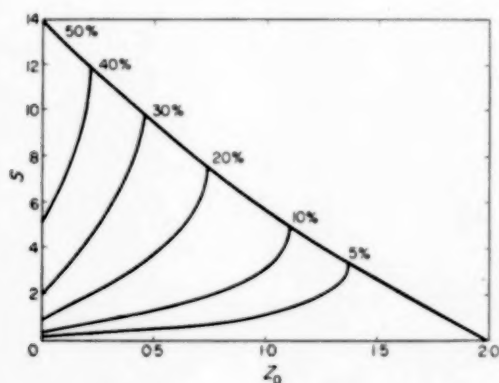
Fig. 3. The optimum yield surface.

then on a is kept constant and equal to a^* until $z_0 = 0$ at J. The locus of the point G at which the change over of policy occurs can be found analytically for the part of the surface originating from III is given by (43) with $a = a_*$. Finally the whole region of interest is bounded by the characteristic $g_S = 0$ whose equation is (44).

The results of an actual calculation are shown in Figs. 3 and 4 for the case $r = 0.5$, $\rho = 5$, $a_* = 0.1$, $a^* = 0.4$. In
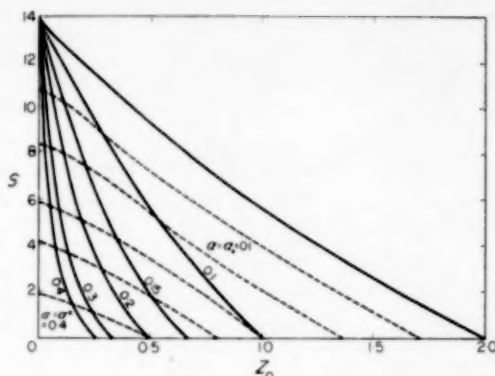

Fig. 4. The optimum temperature policy. (Full lines are of constant a; broken lines show some charateristics).

Fig. 3 the contours of the function $g(z_0, S)$ are shown. From this the maximum yield from a tubular reactor with inlet concentrations x_0, y_0 and holding time S can immediately be obtained as $x_0 g(y_0/x_0, S)$. In Fig. 4 the characteristics and lines of constant temperature policy are shown. From this second figure the policy for any conditions x_0, y_0 and S may be found. We know that the characteristics are reaction paths so that the characteristic from $(z_0 = y_0/x_0, S)$ to the point where it reaches the axis $S = 0$ gives the relation between z_0 and S (i.e. between z and t) down the reactor. The value of a at (z_0, S) gives the optimum inlet temperature and by the principle of optimality the optimum temperature profile must be given by the values of a along the characteristic.
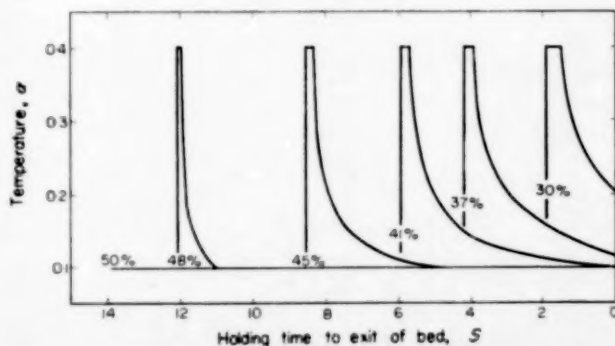

Fig. 5. Temperature profiles for various lengths of reactor and $z_0 = 0$.

Fig. 5 shows some profiles for $z_0 = 0$, that is a feed free of B. The reactor should not in any case have a holding time of more than 13·8 for this would put us in the region of negative g_S. With $S = 13$·8 the optimum profile is to hold the temperature constant at its lowest possible value and the yield is 50 per cent. If the reactor is shorter, say of holding time 12, it is necessary first to have a very short section of maximum temperature followed by a rapidly falling gradient and the rest of the reactor at minimum temperature; the yield is 48 per cent. With shorter reactors the initial section at maximum temperature becomes longer and the falling gradient less steep; the yield falls off accordingly.

Because the absolute optimum for any given z_0 is to have a reaction path on the boundary $g_S = 0$ the optimum policy is to have $a = a_*$ throughout and a reactor of holding time given by (44). In particular for a feed of pure A, the greatest possible yield is

$$g = \left[\frac{b_*}{a_*}\right]^{b_*/(a_*-b_*)} \text{ with } S = \frac{\ln(b_*/a_*)}{b_*-a_*}. \quad (47)$$

This disposes of a paradox suggested by AMUNDSON, that if $E_2 > E_1$ an infinitely long reactor at zero temperature would secure the total conversion of A to B. This is indeed the limit as $a_* \to 0$ and $b_* = \rho a_*^{1/r}$ with $r < 1$, but since temperatures must necessarily be bounded away from absolute zero, equation (47) gives the best that can be done with any particular lower bound a_*.

$r > 1$.

In this case where $E_1 > E_2$ the algebraic manipulations of the preceeding case yield the same equations. However, we must go back to equation (31) to see what they really mean. This equation might be written

$$g_S = \text{Max}\,(aP - a^{1/r}Q)$$

where $P = 1 + (1 + z_0)g_z - g$ and $Q = \rho z_0 (1 + g_z)$. Now in case $r > 1$ the expression on the right hand side, which starts by being zero when $a = 0$, decreases to a minimum and then increases monotonically with a. The formal manipulations find not a maximum, but this minimum so the equations of the last paragraph

give the minimum yield of B. The maximum is to be found by giving a its greatest permitted value a^* provided this makes g_S positive. The known solution (43) applies with $a = a^*$ throughout the region in which $g_S > 0$; this region is given by the equation (44) but with a^* in place of a_*. It thus appears that the doubts that AMUNDSON and BILOUS express as to the validity of their method when $r > 1$, ([2] p. 126), were in fact well founded.

4. THE GENERAL PROBLEM OF AN OPTIMUM TEMPERATURE GRADIENT

We are now in a position to give a general solution of the problem of finding an optimum temperature gradient in a tubular reactor with a number of simultaneous reactions. If n reactions are taking place among $m\,(\geqslant n)$ chemical species it is always possible from stoicheiometric considerations to choose n species and express the concentration of the remainder in terms of these n and the initial concentrations. Let the concentrations of these species be denoted by c_i, $i = 1, 2, \cdots n$, then the kinetic expressions can also be written in terms of these concentrations. A balance over a short section of the reactor then gives

$$\frac{dc_i}{dt} = R_i(c_1, \cdots c_n, T) \quad (48)$$

with the inlet concentrations specified by

$$c_i(0) = c_{i0}. \quad (49)$$

Instead of maximizing the yield of any particular substance we will consider quite a general function $V(c_1, \cdots c_n)$ which will represent the value of the product stream when the concentrations are $c_1, \cdots c_n$. The problem is to find a temperature profile $T(t)$, $0 \leqslant t \leqslant S$, such that $V(c_1(S), c_2(S), \cdots c_n(S))$ is as large as possible. It is again clear that when such a profile has been found the resulting maximum of V is a function of the c_{i0} and S. Let

$$f[c_{10}, \cdots c_{n0}, (S)] = \text{Max}\,V[c_1(S), \cdots, c_n(S)] \quad (50)$$

then by the principle of optimality

$$f(c_{10}, \cdots c_{n0}, S) = \text{Max}\,f(c_1(s), \cdots c_n(s), S-s) \quad (51)$$

for all $s \leqslant S$, where the maximization is over the choice of $T(t)$ in $0 \leqslant t \leqslant s$. By letting $s \to 0$ we arrive at the partial differential equation

$$\frac{\partial f}{\partial S} = \text{Max} \left\{ \sum_{i=1}^{n} \left(\frac{\partial f}{\partial c_{i0}} \right) R_i (c_{i0}, T_0) \right\} \qquad (52)$$

the maximization being over the possible choices of T_0, the inlet temperature. In keeping with a conventional notation for partial differential equations of the first order, let us write

$$c_{i0} = x_i, \quad S = x_{n+1}, \quad \frac{\partial f}{\partial c_{i0}} = p_i, \quad \frac{\partial f}{\partial S} = p_{n+1}.$$

Then the equation (52) is

$$p_{n+1} - \sum_{1}^{n} p_i R_i (x, T_0) = 0. \qquad (53)$$

T_0 being always chosen to maximize the second term. If T_0 is not restricted it must satisfy

$$\sum_{1}^{n} p_i R_i' (x, T_0) = 0 \qquad (54)$$

where R_i' denotes $\partial R_i/\partial T$. If the solution of (54) requires a T_0 outside the acceptable range T_*, T^* then T_0 must be held fixed at one or other of these values. Moreover it is necessary to check that the solution of (54) does correspond to a maximum and not to a minimum. If we denote $\partial R_j/\partial x_i$ by $R_{j,i}$ the characteristic equations of (53) and (54) can be written

$$\frac{dx_i}{d\tau} = - R_i (x, T_0), i = 1, 2, \cdots n, \qquad (55)$$

$$\frac{dS}{d\tau} = \frac{dx_{n+1}}{d\tau} = 1, \qquad (56)$$

$$\frac{df}{d\tau} = \sum_{j=1}^{n} p_j R_j (x, T), \qquad (57)$$

$$\frac{dp_i}{d\tau} = \sum_{j=1}^{n} p_j R_{j,i} (x, T), i = 1, 2, \cdots n, \qquad (58)$$

$$\frac{dp_{n+1}}{d\tau} = 0 \qquad (59)$$

and if T_0 is not held fixed we must add a further equation

$$\frac{dT}{d\tau} = \sum_{i=1}^{n} \sum_{n}^{n} p_j (R_i R_{j,i}' - R_i' R_{j,i}) / \sum_{j=1}^{n} p_j R_j'' \qquad (60)$$

where as before primes denote partial differentiation with respect to T. In general these equations must be solved simultaneously but we notice that if $n = 2$ the ratio p_1/p_2 can be eliminated between equations (54) and (60). In this case it is only necessary to solve three equations, (55) for $i = 1$ and 2 and the modified (60).

The initial values for the integration of these equations come from the condition that

$$f(c_{10}, \cdots c_{n0}, 0) = V(c_{10}, \cdots c_{n0}) \qquad (61)$$

It follows that for a given initial point $c_{i0} = \xi_i$ say, we have for $\tau = 0$

$$x_i = \xi_i, i = 1, 2, \cdots n, x_{n+1} = 0 \qquad (62)$$

$$f = V(\xi_1, \ldots \xi_n), p_i = \partial V/\partial \xi_i, \\ i = 1, 2, \cdots n$$

and p_{n+1} and T_0 are given by

$$p_{n+1} = \sum_{1}^{n} \left(\frac{\partial V}{\partial \xi_i} \right) R_i' (\xi, T_0) \qquad (63)$$

$$0 = \sum_{1}^{n} \left(\frac{\partial V}{\partial \xi_i} \right) R_i' (\xi, T_0) \qquad (64)$$

provided that the solution of (64) lies in the acceptable range T_*, T^*. If it lies below T^* then $T_0 = T^*$ and p_{n+1} is given by (63) with $T_0 = T^*$, if above T^* then $T_0 = T^*$ and we put $T_0 = T^*$ in (63) to give p_{n+1}. Again the value of $p_{n+1} = f_S$ is constant on a characteristic so the region of interest on the initial manifold is bounded by a hypersurface of $[n - 1]$ which can be found from (63) and (64) by setting $p_{n+1} = 0$. Within this region there are three subregions according as the initial value of T_0 is T_*, lies in the range T_*, T^* or is T^*. The integration proceedure is the same as in the previous cases. If it is necessary to start out with T_0 fixed at one of the bounds only the equations (55)–(58) need be integrated, but constant watch is kept on the criterion (54) to see when the optimum T_0 leaves the bound. The integration then continues with the full set of equations (55)–(60) until T_0 reaches the other bound or one of the x_i becomes zero.

5. DISCUSSION

Whilst the preceeding section gives a method of finding the optimum temperature gradient in quite

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a general case there are other questions that come to mind. If for example we include the cost of constructing and maintaining a reactor of holding time S, then a new profit function should be used which takes this into account. Suppose that this cost is a function $C(S)$ then we might take a profit function $P = V[c_1(S), \cdots c_n(S)] - C(S)$ and seek to maximize this. Here we are going to choose not only $T(t)$, $0 \leqslant t \leqslant S$, but also S itself and the optimum when these choices are made will be a function only of $c_{10}, c_{20}, \cdots c_{n0}$, say $g(c_{10}, \cdots c_{n0})$. This problem can be solved by the method of the previous paragraph. All we need do is to keep track of

$$\frac{dP}{dS} = \Sigma \frac{\partial V}{\partial c_i} R_i - C'(S)$$

in the integration along the characteristic lines and stop as soon as this derivatives reaches zero. The value of S at which this step is made will be a function of the c_{i0}, $i = 1, \cdots n$, there, say $S \sigma(c_{10}, \cdots c_{n0})$. Then $g(c_{10}, \cdots c_{n0}) = f(c_{10}, \cdots c_{n0}, \sigma) - G(\sigma)$.

We have not said anything as to the possibility of actually attaining a given profile. If Q is the rate of heat removal per unit length from the tubular reactor and c_p and ρ the specific heat and density of the reaction mixture a heat balance gives

$$c_p \rho \frac{dT}{dt} = \sum_{i=1}^{n} H_i R_i(c, T) - Q \qquad (65)$$

where the H_i are suitably defined heats of reaction. From the required profile Q may be calculated as a function of t from this equation. In view of the rather steep gradients that may be demanded for optimum working the values of Q may become too large for normal engineering practice to handle. It would therefore be of value to find an optimum design for which Q should not exceed some maximum, $Q \leqslant Q^*$. This can be done by varying the upper limit of permitted temperature T^*. The maximum value of Q will be a function of T^*, say $Q_m(T^*)$, and this may be determined quite readily for several T^*. The solution is then given by choosing the T^* that makes $Q_m(T^*) = Q^*$. Alternatively the value of Q at each point of a given trajectory may be

calculated from (65) during the course of the integration. Then as soon as Q reaches the value Q^* the temperature T must not exceed the value it has then reached. By suddenly requiring the temperature to be constant, i.e. the left hand side of (65) to be zero, a discontinuity in Q is produced which lowers it below the maximum permitted value Q^*.

If a tubular reactor with a definite cooling system, such as co- or counter-current tube cooling, is to be designed for optimum yield by choosing the correct inlet temperature and area of cooling tube we are actually faced with a much more difficult problem than choosing the whole temperature profile. This is because the problem is too determinate, and fixing the inlet temperature and the cooling tube area fixes the whole temperature profile. It is hoped to discuss this type of problem elsewhere.

Finally it should be evident that other features of tubular reactors can be considered by the methods of dynamic programming. With gas reactions the pressure will be an important variable and we would work with partial pressures rather than concentrations. With catalytic reactions there is also the possibility of varying the grade of catalyst and its selectivity throughout the bed. This problem can also be treated by dynamic programming.

Notation

$A(a) = db/da$

a = rate constant of $A \rightarrow B = k_1 \exp(-E_1/RT)$

$B(a) = (b - Aa)/A'$

b = rate constant of $B \rightarrow C = k_2 \exp(-E_2/RT)$

c_i = concentration $i = 1, 2, \cdots n$

$C(S)$ = cost of reactor of length S

$F(x)$ = dependence of rate $A \rightarrow B$ on concentration of A

$f(x_0, y_0, S)$ = optimum yield from reactor of holding time S

$G(y)$ = dependence of rate of $B \rightarrow C$ on concentration of B

$g(z_0, S) = f(x_0, y_0, S)/x_0$

k_i = constants in reaction rates a and b

n = number of reactions

P = profit

Q = rate of heat removal
$r = E_1/E_2$
$R = r/(1 - r)$
R_i = rate of ith reaction
S = total holding time of reactor
t = current holding time along tubular reactor
T = temperature

$V(c)$ = value of product
x = concentration of A
y = concentration of B
$z = x/y$
$\beta(a) = (b - a)/ra^2$
$\rho = k_2 k_1^{-1/r}$
τ = variable along characteristics

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Diffusion within a developing boundary layer — a mathematical solution for arbitrary velocity distribution

F. O. MIXON and J. J. CARBERRY

Engineering Research Laboratory, Engineering Department, E. I. du Pont de Nemours & Co., Inc.,
Wilmington, Delaware.

Abstract—A solution is presented for the diffusion of heat or mass within a developing laminar boundary layer in which the velocity is described in terms of directional components, each raised to an arbitrary power. Reduction of the general solution to specific cases is demonstrated. The Schmidt or Prandtl number exponent must be between values of $\frac{1}{2}$ and $\frac{2}{3}$ depending on the ratio of the concentration to hydrodynamic boundary layer thickness.

Résumé—Les auteurs étudient la diffusion de chaleur ou de mass à l'interiéur d'une couche limite laminaire en formation; la vitesse est exprimée en fonction des composantes spatiales affectées d'une puissance arbitraire. Ils montrent comment passer de la solution générale aux cas particuliers. Les exposants des nombres de Prandtl et de Schmidt doivent être compris entre $\frac{1}{2}$ et $\frac{2}{3}$ suivant le rapport de l'épaisseur de la couche limite de concentration ou de température, à l'épaisseur de la couche limite hydrodynamique.

Zusammenfassung—Es wird eine Lösung angegeben für Stoff- oder Wärmediffusion innerhalb einer sich entwickelnden laminaren Grenzschicht, in der die Geschwindigkeit durch Richtungskomponenten dargestellt wird, die durch je eine übergeordnete Kraft hervorgerufen werden. Die Anwendung der allgemeinen Lösung auf spezielle Fälle wird aufgezeigt. Der Exponent der Schmidt- oder Prandt-Zahl, der von dem Verhältnis der Konzentration zur Dicke der hydrodynamischen Grenzschicht abhängt, muss sich dabei zwischen $\frac{1}{2}$ und $\frac{2}{3}$ bewegen.

WHEREAS the process of diffusion within a laminar boundary layer has been analysed extensively for cases involving various velocity distributions [1, 2], the general instance in which the velocity at the fluid–solid boundary is described in terms of x and y raised to arbitrary powers, b and a respectively, would appear to be worthy of analysis. Thus the velocity relative to that at the boundary-layer edge is assumed to be of the form

$$U/U_\infty = K \left[(U_\infty y/\nu)^a / (U_\infty x/\nu)^b \right] \quad (1)$$

where the variables x and y are being expressed as Reynolds numbers in the direction of flow and perpendicular thereto.

The diffusive process is considered to be one of heat or mass transfer which may be described by the equation

$$V \frac{\partial c}{\partial y} + U \frac{\partial c}{\partial x} = D \left[\frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial x^2} \right]. \quad (2)$$

The following simplifications are now imposed:

(1) Constancy of physical properties.
(2) A negligible contribution of the terms $V(\partial c/\partial y)$ and $\partial^2 c/\partial x^2$.

The error involved in neglecting the perpendicular component of velocity will be discussed later.

The boundary conditions are

$$c(0, y) = c_\infty$$
$$c(x, 0) = c_W$$
$$c(x, \infty) = c_\infty$$

The equation to be solved is then

$$K \frac{Y^a}{X^b} \frac{\partial c}{\partial X} = \left(\frac{D}{\nu} \right) \frac{\partial^2 c}{\partial Y^2}. \quad (3)$$

where

$$X = x U_\infty / \nu$$

$$Y = y U_\infty / \nu.$$

SOLUTION

Let $z = X^m Y^n$

Therefore $A(z) = c(X, Y) = A(X^m Y^n)$.

Performing the necessary differentiation and substituting into equation (3) yields

$$KmX^{-b-1} Y^{a+2} \frac{dA}{dz} =$$

$$\left(\frac{D}{\nu}\right) \left[\frac{dA}{dz} n(n-1) + \frac{d^2A}{dz^2} n^2 X^m Y^n \right] \quad (4)$$

For

$$m = -b - 1$$
$$n = a + 2,$$

equation (4) reduces to

$$z \frac{d^2A}{dz^2} = (\alpha z + \beta) \frac{dA}{dz} \quad (5)$$

where

$$\alpha = Km/n^2 P$$
$$\beta = -(n-1)/n$$

and $\quad P = \dfrac{\nu}{D} = $ fluid properties group

Letting $p = dA/dz$ and integrating, one obtains

$$dA/dz = C e^{\alpha z} z^\beta$$

The constant C is obtained by further integration over the entire range of the variable z. Thus

$$\Delta A = A(z = \infty) - A(z = 0) = C \int_0^\infty e^{\alpha z} z^\beta \, dz \quad (6)$$

Recognizing that the integral on the right-hand side of equation (6) is of the form of the gamma function, Γ, one finds that

$$C = \frac{\Delta A (-\alpha)^{\beta+1}}{\Gamma(\beta+1)} \quad (7)$$

Therefore

$$\frac{dA}{dY} = \frac{\Delta A (-\alpha)^{\beta+1}}{\Gamma(\beta+1)} e^{\alpha z} z^\beta n X^m Y^{n-1}$$

The net diffusive flux at the boundary, $y = 0$, then becomes, in terms of x and y,

$$D \frac{\partial c}{\partial y}\bigg|_{y=0} = \Delta c \left[\frac{(-\alpha)^{\beta+1}}{\Gamma(\beta+1)}(a+2) \right.$$

$$\left. \left(\frac{U_\infty x}{\nu}\right)^{(-b-1)/(a+2)} \left(\frac{U_\infty}{\nu}\right) D \right] \quad (8)$$

Since $\quad -D \dfrac{\partial c}{\partial y}\bigg|_{y=0} = k \Delta c$

then the instantaneous value of the transfer coefficient, k, is the bracketed expression in equation (8).

The average transfer coefficient may be expressed in terms of the exponents a and b, the Schmidt or Prandtl number, $P = \nu/D$, and the length Reynolds number, $\mathrm{Re} = U_\infty x/\nu$, as

$$\bar{k} = \frac{\left[K(b+1)/(a+2)^2 \right]^{1/(a+2)} \cdot (a+2)^2}{\Gamma[1/(a+2)](a-b-1)}$$

$$U_\infty (P)^{(-a-1)/(a+2)} (\mathrm{Re})^{(-b-1)/(a+2)} \quad (9)$$

DISCUSSION

A number of cases pertinent to the science of chemical engineering following by specification of the exponents, a and b.

Case 1

The velocity is invariant in x and y, that is

$$a = b = 0 \text{ and } K = 1$$

$$\bar{k} = \frac{4}{\Gamma(1/2)} \left(\frac{D}{4(x/U)}\right)^{1/2} = 2\sqrt{\frac{D}{\pi\theta}} \quad (10)$$

which is the HIGBIE [3] relation for the average transfer coefficient, where $x/U = \theta$, the time of transient diffusion.

Case 2

The velocity is a simple linear function of y and independent of x, that is

$$a = 1, \quad b = 0, \quad K = (\nu/y_0 U_a)$$

This specification will be recognized as the LEVEQUE [4] approximation for heat transfer between the wall of a conduit of diameter $2y_0$, and a fluid in laminar flow, where the average velocity is U_a. In this instance equation (9) reduces to

$$\bar{k} = 1 \cdot 615 \left(\frac{D^2 U_a}{2y_0 x}\right)^{1/3} \quad (11)$$

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In terms of the Nusselt number,

$$\text{Nu} = \bar{k}\, 2y_0/D = 1\cdot615\left(\frac{U_a\,(2y_0)^2}{xD}\right)^{1/3} \quad (12)$$

Equation (12) is identical to that derived by Léveque [4] and by Marshall and Pigford [5].

Case 3

The velocity is a function of both x and y, in a fashion dictated by laminar boundary layer theory. That is

$$a = 1, \quad b = 1/2$$

and the velocity distribution becomes

$$U/U_\infty = K\, y/\sqrt{\frac{ux}{U_\infty}} = K\,\eta \quad (13)$$

The term K_η will be recognized as the first, linear term of the various power series often employed to describe the velocity distribution within a laminar boundary layer on a flat plate. Equation (9) becomes, in this case,

$$\bar{k} = 0\cdot817\, U_\infty\, P^{-2/3}\, \text{Re}^{-1/2} \quad (14)$$

Equation (14) has been successfully employed in the prediction of fluid-particle mass transfer in fixed beds (6), by defining the distance over which the boundary layer develops in terms of the particle diameter.

The error involved in ignoring the term $V(\partial c/\partial y)$ in the above development may be assessed by a comparison of equation (14) with the result found when this term is included. Following Schlichting [2]

$$\frac{c - c_\infty}{c_w - c_\infty} = 1 - 2\epsilon + 2\epsilon^3 - \epsilon^4 \quad (15)$$

where

$$\epsilon = y/\delta_a$$
$$\delta_a/\delta = P^{-1/3} \text{ and } \delta = 5\cdot83\sqrt{\frac{ux}{U_\infty}}. \quad (16)$$

Differentiating (15) to obtain the flux at $y = 0$, and solving for $\bar{k}$ in a manner comparable to that outlined earlier, one obtains

$$\bar{k} = 0\cdot687\, U_\infty\, P^{-2/3}\, \text{Re}^{-1/2} \quad (17)$$

Hence, the error involved by the assumption underlying equation (14) is about 20 per cent.

SCHMIDT OR PRANDTL NUMBER FUNCTIONALITY

Equation (9) states that the exponent on the Schmidt or Prandtl number must lie between $\frac{1}{2}$ and $\frac{2}{3}$. It seems reasonable to suppose that Case 1 above, in which the velocity is invariant in x and y, corresponds to that circumstance in which the major resistance to the transport process lies outside the hydrodynamic boundary layer. This behaviour may be expected when the diffusivity is rather high (low Schmidt or Prandtl number). On the other hand Case 3 corresponds to the instance wherein the major resistance lies within that portion of the boundary layer which can be represented by the linear approximation stated in equation (13).

It is of interest to inquire into the exact nature of the fluid property number dependency as a function of the ratio of the concentration or thermal to the hydrodynamic boundary layer thicknesses.

This ratio is defined as

$$\Delta = \delta_a/\delta,$$

where according to Schlichting [2], Δ is specified in terms of the property group P as

$$\Delta^2\, H(\Delta) = \frac{37}{315}\frac{1}{P} \quad (18)$$

and

$$H(\Delta) = \frac{2}{15}\Delta - \frac{3}{140}\Delta^3 + \frac{1}{180}\Delta^4 \text{ for } \Delta < 1$$

and

$$H(\Delta) = \frac{3}{10} - \frac{3}{10}\frac{1}{\Delta} + \frac{2}{15}\frac{1}{\Delta^2} - \frac{3}{140}\frac{1}{\Delta^4} +$$
$$\frac{1}{180}\frac{1}{\Delta^5}, \text{ for } \Delta > 1 \quad (19)$$

(The third term in the latter equation is erroneously printed as $9/15\,(1/\Delta^2)$ in the Schlichting text.)

A plot of the solution to the above equations is shown in Fig. 1, which indicates that the property number exponent tends toward a limiting value of $\frac{1}{2}$ at values of that group of less than $1\cdot0$. In terms of $\bar{k}$,

$$\bar{k} = 0\cdot817\, U_\infty\, P^{-2/3}\, \text{Re}^{-1/2} \quad P > 1\cdot0$$
$$\bar{k} = 1\cdot26\, U_\infty\, P^{-1/2}\, \text{Re}^{-1/2} \quad P < 0\cdot05$$

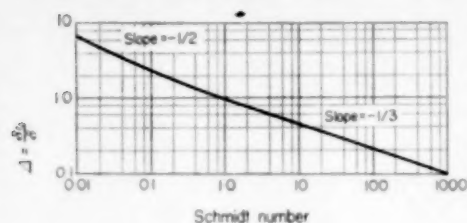Chem. Engng. Sci. Vol. 13, No. 1. August 1960.

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FIG. 1. Ratio of concentration to hydrodynamic boundary layer thickness as a function of Schmidt number.

It may be concluded that in the property value regime of from 0·05 to 1·0 no unique exponent upon the Schmidt or Prandtl number prevails.

NOTATION

A	Transformed concentration variable
a, b	Exponents in equation (1)
c	Concentration of diffusing substance
C	Constant defined by equation (7)
D	Diffusivity
$H(\Delta)$	Function defined by equations (19)
$\bar{k}$	Average transfer coefficient, equation (9)
K	Coefficient in equation (1)
m, n	Exponents in equation (4)
P	Schmidt or Prandtl number
p	dA/dz
U	Point velocity
U_a	Average velocity
U_∞	Velocity at boundary layer edge
V	Normal component of velocity
x, y	Distance variables
X, Y	Transformed variables defined in equation (3)
z	Transformed variable, $X^m Y^n$
α, β	Defined by equation (5)
η	$y/\sqrt{\dfrac{\nu x}{U_\infty}}$
Γ	Gamma function
θ	Time
ϵ	y/δ_a
δ_a	Concentration or thermal boundary layer thickness
δ	Hydrodynamic boundary layer thickness

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Perforated-tube flowmeter

P. V. Danckwerts and A. K. Sikder

Department of Chemical Engineering, Imperial College, London S.W.7

Abstract—A cheap and simply-constructed visual flow-meter is described. It consists of a Rotameter-type bob fitting fairly closely inside a perforated tube. Most of the fluid flows out of the holes below the bob; the height of the bob indicates the flow-rate. A simple theoretical treatment is given. Following experiments with air and water, formulae are given which can be used to specify the leading dimensions of a meter for a given duty.

Résumé—Les auteurs décrivent un débitmètre à lecture directe facile à réaliser et peu coûteux. Il consiste en un flotteur du type Rotamètre bien ajusté dans un tube perforé. La plus grande partie du fluide s'écoule par les trous au-dessous du flotteur. La hauteur du flotteur indique la vitesse d'écoulement. Suit une étude théorique simple. Après des expériences avec l'air et l'eau, les auteurs donnent des formules pouvant être utilisées pour trouver les dimensions essentielles d'un appareil de mesure pour une plage déterminée.

Zusammenfassung—Ein billiges Durchflussmessgerät einfacher Konstruktion wird beschrieben. Es besteht aus einem Schwimmer vom Rotameter-Typ mit geringem Spiel innerhalb eines perforierten Rohres. Der grösste Teil des strömenden Mediums fliesst durch die Löcher unterhalb des Schwimmers aus. Die Höhe des Schwimmers zeigt die Durchflussgeschwindigkeit an. Eine einfache Erläuterung der theoretischen Grundlagen wird angegeben. Aufgrund von Experimenten mit Luft und Wasser werden Formeln entwickelt, die zur Berechnung der Hauptabmessungen eines Messgerätes für eine bestimmte Durchflussleistung dienen können.

THE instrument described here is a simple visual flow-meter, which can be constructed from cheap materials without the need for any precision machining.

DESCRIPTION OF FLOWMETER

The flowmeter is shown diagrammatically in Fig. 1. It consists of two concentric transparent tubes. The inner one is made of plastic (e.g. Perspex) and perforated by a regular array of holes. A " bob," similar to that used in a Rotameter, is suspended by the stream of fluid in the central tube. A proportion of the fluid (depending on the closeness of fit of the bob) leaks past the bob; the remainder flows out through the holes in the central tube. The height of the top of the bob indicates the flow-rate of the fluid.

A cross-wire is fitted to the top of the inner tube, to prevent the bob from being blown out, and a coiled-spring arrester at the bottom. A wire spacer can be fitted to keep the two tubes concentric. The inner tube must be vertical, but this setting is not critical unless the bob is a very close fit.
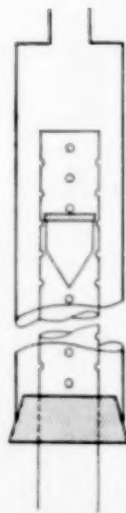

FIG. 1. Flow meter.

Thick-walled Perspex tubes tend to crack after drilling. This can be prevented by annealing at 70°C for a few hours.

A sphere can be used instead of a Rotameter-type bob, but is usually less satisfactory because of instability. It would be more satisfactory in principle to have a continuous opening in the walls of the central tube rather than a series of holes. Vertical and spiral slits were tried, but neither were satisfactory. It seems that non-precision methods of fabrication do not produce slits of uniform width and finish, and that the slit may widen, temporarily or progressively, if the inner tube bulges under pressure.

The minimum flow-rate which can be measured is that which leaks past the bob; this can be made smaller by making the bob a closer fit in the tube. The range of the instrument depends on the weight of the bob and the number and diameter of the holes. If the bob is hollowed-out its weight can be varied by putting in fine lead shot. The accuracy depends on the size of the holes; other things being equal, twice as many holes, each of half the cross-sectional area, will roughly halve the average error.

EXPERIMENTAL

Experiments were carried out with air and water, using a variety of tubes and bobs; in most cases the latter were hollow and weighted with varying amounts of fine lead shot. Typical results are shown in Fig. 2. Table 1 shows the range of variables covered.
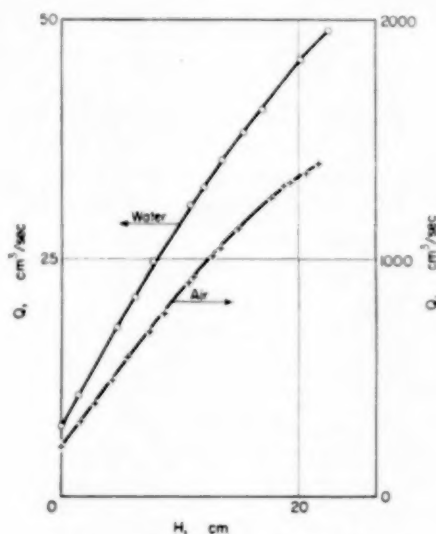

FIG. 2. Typical calibration curves.

Water	Air
$N = 6\cdot3$ cm^{-1}	$N = 6\cdot3$ cm^{-1}
$d = 1\cdot275$ cm	$d = 1\cdot275$ cm
$A = 0\cdot011$ cm^2	$A = 0\cdot011$ cm^2
$D = 1\cdot19$ cm	$D = 1\cdot19$ cm
$W/981 = 2\cdot35$ g wt	$W/981 = 1\cdot39$ g wt

Table 1. *Showing range of variables covered*

N (cm^{-1})	d (cm)	D (cm)	A (cm^2)	Fluid	$W/981$ (Weight of bob immersed in fluid) (g wt.)	Q (Max. values measured) (cm^3/sec)	Q_0 (cm^3/sec)
6·3	0·635	0·55	0·011	water air	0·17–0·68 0·26–0·76	12–34 480–770	2·4–5 120–130
6·3	1·275	1·14	0·011	water air	0·83–1·56 1·29–1·82	30–45 1330	8–11 310–368
		1·19	0·011	water air	0·90–2·55 1·39–2·18	27–44 1330	4–8 224–343
			0·00126	air	1·39–2·55	340–440	217–281

Comparison with Theory

The rate of leakage, Q_0, past the bob will be the same (for a given fluid) at all flow-rates. Following the conventional treatment for the Rotameter, we have

$$\frac{Q_0 D}{d^2 - D^2} \sqrt{\frac{\rho}{W}} = K, \qquad (1)$$

where D and d are the bob and tube diameters respectively, ρ the density of the fluid and W the submerged weight of the bob (force units). K is related to the discharge coefficient for flow past the bob; for all the experiments discussed here the value of K was found to be between 0·8 and 1·2.

The non-linearity of the relation between the flow-rate, Q, and the height of the bob, H (see Fig. 2) is due mainly to the fact that the fluid in the central tube decelerates as it flows upward, and that its pressure therefore rises. A simplified analysis is given in the Appendix, and leads to the relation

$$2 \frac{Q' D}{d^2} \frac{k\rho}{\pi W} = \sin\left(\frac{4CNAH}{\pi d^2}\right), \qquad (2)$$

where $Q' = Q - Q_0$ is the total flow-rate through the holes beneath the bob, N the number of holes per unit height and A the area of one hole. C is the discharge-coefficient for the holes below the bob, and k a constant relating to pressure-recovery due to decleration. This relationship, with $C = 1$ and $k = 1$, is compared with certain of the experimental curves in Fig. 3; the remaining experimental curves, for each hole diameter, lie between the curves shown. It will be seen that the results conform broadly to the " theoretical " expression, equation (2) above. The expression

$$1·5 \frac{Q' D}{d^2} \sqrt{\frac{\rho}{\pi W}} = \sin\left(\frac{2NAH}{\pi d^2}\right)$$

(corresponding to $C = 0·5$, $k = 0·56$) fits all the experimental curves to within a factor of 1·5 over most of the range.

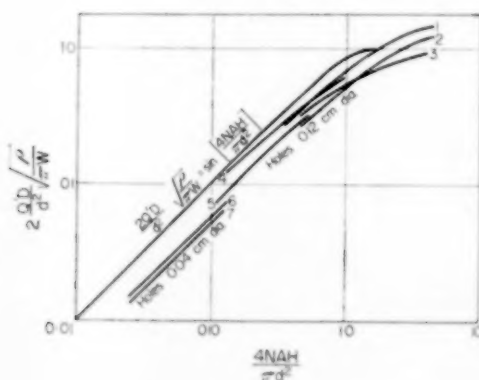Equation (2) implies that at a certain flow-rate, given by

Fig. 3. Experimental results.

Curve	Fluid	N (cm^{-1})	d (cm)	D (cm)	A (cm^2)	$W/981$ (g wt.)
1	water	6·3	0·635	0·546	0·011	0·675
2	air	6·3	0·635	0·537	0·011	0·259
3	water	6·3	0·635	0·546	0·011	0·170
4	air	6·3	1·275	1·19	0·011	1·90
5	air	6·3	1·275	1·14	0·011	1·82
6	air	6·3	1·275	1·19	0·00126	1·94
7	air	6·3	1·275	1·19	0·00126	1·39

$$Q_{max} = \frac{d^2}{2D}\sqrt{\frac{\pi W}{k\rho}}, \qquad (3)$$

the bob will be blown right up the tube, no matter how long the latter may be. This condition is approached by certain of the curves in Fig. 3.

Conclusions

The following expressions may be used to calculate approximately the leading dimensions of a perforated-tube flowmeter for a given duty, at least so long as conditions do not depart too widely from those described. Final adjustments are easily made by adding lead shot to the bob.

$$Q = Q_0 + Q'. \qquad (4)$$

where $\qquad Q_0 \simeq \dfrac{d^2 - D^2}{D}\sqrt{\dfrac{W}{\rho}}; \qquad (5)$

$$Q' \simeq 0.67 \frac{d^2}{D}\sqrt{\frac{\pi W}{\rho}} \sin\left[\frac{2NAH}{\pi d^2}\right]. \quad (6)$$

It follows from equation (6) that the relationship between Q and H will be almost linear at lower flow-rates (when $2NAH/\pi d^2 < 0.5$, i.e. when the area of the holes below the bob is less than the cross-section of the tube).

$$\left.\begin{array}{l} Q' \simeq 1.33 \dfrac{NAH}{D}\sqrt{\dfrac{W}{\pi\rho}}; \\[2mm] NAH < \pi d^2/4. \end{array}\right\} \qquad (7)$$

There is an upper limit, Q_{max}, to the flow-rate which can be measured, regardless of the length of the tube:

$$Q_{max} \simeq Q_0 + 0.67 \frac{d^2}{D}\sqrt{\frac{\pi W}{\rho}}. \qquad (8)$$

Acknowledgements—Our thanks are due to Professor A. Acrivos for helpful comments, and to Mr. A. C. V. Sweeting and the workshop staff for their help and interest.

Appendix

The general problem of flow in uniformly-tapped pipes is a difficult one; a much simplified treatment is used here.

The following approximations are made:

1. Wall-friction is neglected;
2. The discharge coefficient through each hole below the bob is taken to be the same;

3. The velocity below the bob is regarded as negligible compared with that at the entrance to the inner tube;
4. The bob is regarded as simply a flat disk, its position in the tube being that of the top of the real bob;
5. It is assumed that pressure-recovery due to deceleration in the inner tube can be expressed by

$$dP = - k\rho d\,(u^2) \qquad (9)$$

where k is a constant of order of magnitude unity [1].

6. The pressure in the space between the inner and outer tubes and above the bob is taken to be uniformly equal to P_0.

Let the pressure in the inner tube at a height h above the level at which the perforations begin be P. Then the rate of discharge through each hole at this level (from assumption 2) is

$$CA\sqrt{\left[\frac{2}{\rho}(P - P_0)\right]}$$

where A is the area of each hole and C the discharge coefficient. Then, if q is the residual vertical flow in the inner tube at height h, and N the number of holes per unit height,

$$\frac{dq}{dh} = - CNA\sqrt{\left[\frac{2}{\rho}(P - P_0)\right]}. \qquad (10)$$

The pressure P' at height H (just below the bob) must be sufficient to support the weight of the bob, so

$$\frac{\pi D^2}{4}(P' - P_0) = W \qquad (11)$$

where D is the diameter of the bob. The linear velocity u in the tube is related to q by

$$q = \frac{\pi d^2 u}{4}. \qquad (12)$$

Substituting for u in equation (9), and integrating between h (an arbitrary height) and H, we have

$$\int_P^{\left(\frac{4W}{\pi D} + P_0\right)} dP = - K\rho\left(\frac{4}{\pi d^2}\right)^2\int_q^0 d\,(q^2),$$

whence $\qquad P - P_0 = \dfrac{4W}{\pi D^2} - K\rho\left(\dfrac{4q}{d\pi^2}\right)^2. \quad (13)$

Substituting this expression for $(P - P_0)$ in equation (10), and integrating between O and H, we obtain an expression for the total rate of flow, Q', through the holes:

$$- CNA \int_0^H dh = \int_{Q'}^0 \frac{dq}{\sqrt{[(8W/\pi D^2 \rho) - 2K\,(4q/\pi d^2)^2]}},$$

whence

$$2\frac{Q'D}{d^2}\frac{K\rho}{\pi W} = \sin\frac{4CNAH}{\pi d^2}. \tag{14}$$

(In setting the upper limit of the right-hand integral equal to 0, we are introducing assumption 3).

This treatment is easily extended to take into account the acceleration of the fluid in the annular space between the inner and the outer tubes, which is ignored in assumption 6. The left-hand side of equation (14) should be multiplied by a factor which is approximately

$$\sqrt{\left(1 + \frac{a^2_1}{a^2_2}\right)}.$$

where a_1 is the cross-sectional area of the inner tube and a_2 that of the annulus. In the experiments described here the correction never amounted to more than about 1 per cent.

NOTATION

A	Area of hole
a_1	Cross-sectional area of perforated tube
a_2	Cross-sectional area of annulus between tubes
C	Discharge coefficient for hole (equation 10)
d	Interior diameter of tube
D	Maximum diameter of bob
h	Height above lowest hole
H	Height of top of bob above lowest hole
K	Constant in equation (1)
k	Constant in equation (9)
N	Number of holes per unit height
P	Pressure
P_0	Pressure outside tube and above bob
P'	Pressure at height H
q	Vertical flow-rate at height h
Q	Total flow-rate
Q_0	Flow-rate past bob
Q'	Flow-rate through holes
u	Velocity through holes
W	Submerged weight of bob (force units)
ρ	Density of fluid

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Shorter Communications

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Note on a method for computing the effect of temperature on reaction yields

RASTOGI and DENBIGH [1] have pointed out that the effect of temperature on the yield of a chemical reaction which is not allowed to proceed to equilibrium is quite different from the effect of temperature on the equilibrium yield. To compute this effect in a particular case they have integrated the rate equation which describes the detailed kinetics of their example. Subsequent elementary manipulations yield an expression for $r = (d\lambda/dT)/(d\lambda_e/dT)$ which may be as high as 10 for $\lambda/\lambda_e = 0.9$. Here λ is the degree of advancement of the reaction at a fixed time, and λ_e is the degree of advancement at equilibrium.

The object of this note is to develop an approximation which enables one to effect a quite considerable simplification in the calculation of r by circumventing the solution of the compilcated differential equations which describe the reaction kinetics. The subsequent calculations also become appreciably simpler and the cost in accuracy is slight.

We write the chemical reaction in question as

$$\sum_{a=1}^{s} \nu_a X_a = 0 \qquad (1)$$

X_a stands for 1 mole of component α and ν_a is the stiochiometric coefficient of α. Stoichiometric coefficients are taken as positive for products and negative for reactants, Denoting the molar concentration of component α by n_a, the degree of advancement, λ, is defined by

$$dn_a = \nu_a \, d\lambda \qquad (2)$$

The constant of integration implied by equation (2) is determined by setting $\lambda = 0$ at the initiation of the reaction. The rate equation is written

$$\frac{d\lambda}{dt} = g(n_a, T) \qquad (3)$$

where T is the absolute temperature. The form of g depends on the particular reaction under investigation.

The approximation considered here is the utilization of the observation that not too far from equilibrium $g(n_a, T)$ can be expanded about its equilibrium value of zero, and only the term linear in λ retained [2]. Thus we write approximately

$$\frac{d\lambda}{dt} = \frac{-(\lambda - \lambda_e)}{\tau}$$

$$\frac{1}{\tau} = -\sum_a \nu_a \left(\frac{\partial g}{\partial n_a} \right)_e \qquad (4)$$

where the subscript e indicates that the derivative is to be evaluated for the equilibrium values of the n_a. The relevant solution of equation (4) is

$$\lambda = \lambda_e \left[1 - \exp\left(-\frac{t}{\tau} \right) \right] \qquad (5)$$

Writing $\lambda/\lambda_e = f$, simple differentiation yields

$$\frac{d\lambda/dT}{d\lambda_e/dT} = r = f - \frac{(1-f)\ln(1-f)(d\ln\frac{1}{\tau}/dT)}{d\ln\lambda_e/dt} \qquad (6)$$

$(d\ln\lambda_e/dT)$ may be determined by thermodynamics, $(d\ln\frac{1}{\tau}/dT)$ depends on the mechanism of the reaction under investigation.

As an example we consider the reaction also chosen by RASTOGI and DENBIGH

$$X_3 + X_4 - X_1 - X_2 = 0 \qquad (7)$$

with $n_1(0) = n_2(0) = a$, $n_3(0) = n_4(0) = 0$. Assuming the rate law is

$$\frac{d\lambda}{dt} = k_1(n_1 n_2 - K^{-1} n_3 n_4) \qquad (8)$$

where K is the equilibrium constant, the relaxation time is given by

$$\frac{1}{\tau} = 2ak_1 K^{-1/2} \qquad (9)$$

and

$$\lambda_e = \frac{aK^{1/2}}{1 + K^{1/2}} \qquad (10)$$

Then from equation (6), the van't Hoff equation and the Arrhenius equation,

$$r = f - 2(1-f)\ln(1-f)(1+K^{1/2})\left(\frac{E}{\Delta H} - \frac{1}{2} \right) \qquad (11)$$

where E is the activation energy for the forward reaction, and ΔH is the enthalpy change of the reaction. Numerical results are given in Table 1. The results of RASTOGI and DENBIGH obtained by exact integration of the rate equation are also tabulated for comparison. Note that we do not consider values of f less than 0.9, for our considerations yield a reasonable approximation only near equilibrium.

Table 1 also gives calculations for two other rate laws, together with values determined by exact integration.

Table 1. Comparison of r computed by present method [r (present)] with r computed by the exact method of Reference 1. [r (exact)].

Reaction	$H_2 + I_2 \rightleftharpoons 2HI$		cis $\rightleftharpoons$ trans $CH_3 - CH = CHCH_3$		$CH_3CO_2C_2H_5 \rightleftharpoons (H_2O)$ $CH_3COOH + C_2H_5OH$	
Kinetic type	Bimolecular– bimolecular		Unimolecular– unimolecular		Unimolecular– bimolecular [4]	
E (Kcal)	44 [3]		18 [8]		14·9 [7]	
H (Kcal)	3 [3]		0·950 [8]		0·890 [6]	
K	0·0022 [3]		1·12 [8]		0·005 [5]	
T (°K)	764		620		298	
		r (present)	r (exact)	r (present)	r (exact)	r (present)	r (exact)

f		r (present)	r (exact)	r (present)	r (exact)	r (present)	r (exact)
	0·99	2·49	2·86	2·8	2·8	2·64	2·88
	0·95	5·80	7·0	6·8	6·8	6·45	—
	0·90	8·40	10·6	9·9	9·9	9·3	10·8

Numbers in brackets are literature references.

In the case of opposing uni-molecular reactions the approximation we use is in fact exact since the actual rate equation is linear to start with. In all cases shown the approximate calculations yield numbers in tolerable agreement with the exact calculation.

The method presented here can be extended without difficulty to cases where several competitive reactions occur simultaneously. The differential equations are again trivial, but the subsequent algebra is quite complicated and the results do not appear to be in a particularly useful form. In addition, the method can be used to treat the effect of other parameters such as pressure on reaction yields. Such effects were also discussed by RASTOGI and DENBIGH. No new features are introduced by considering pressure rather than temperature, so we shall not go into details. The numerical aggreement with the more exact treatment of RASTOGI and DENBIGH is about the same as in the temperature case.

NOTATION

n_α = molar concentration of component α

v_α = stoichiometric coefficient of component α in a reaction

k_1 = forward rate constant

K = equilibrium constant

λ = progress variable of a chemical reaction

τ = relaxation time of a chemical reaction

E = activation energy for the forward reaction

ΔH = enthalpy change

f = fractional attainment of equilibrium

r = ratio of $(d\lambda/dT)$ at fixed time to $(d\lambda_e/dT)$

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California Institute of Technology,
Pasadena, California.

W. G. LAIDLAW
R. M. MAZO

Book Reviews

Polymer. Butterworths Scientific Publications, London. Published quarterly. Annual subscription £5, $15.00.

DURING the last twenty years, with the growth in importance of the chemistry and technology of polymers, the need for an outlet for the large volume of published matter on these topics has become clear. The need was recognised some fifteen years ago in America with the appearance of the *Journal of Polymer Science* and more recently with the addition of the *Journal of Applied Polymer Science*, by which it is hoped to separate the more fundamental and applied aspects. "*Polymer*," a new journal produced by Butterworths Scientific Publications, is designed to cover both these aspects and its choice of editorial board should go far towards achieving a sound balance. The journal is to appear quarterly and the first part of Vol. I comprising some 120 pages, has just appeared. Containing twelve full papers on the chemistry and physics of a variety of polymers, in solution and otherwise, and on polymerization processes, as well as short letters and three book reviews, the objectives of the journal are satisfactorily reached in this issue. Nor should it be difficult to maintain this level from the large amount of relevant work which is proceeding in industry, research institutions and university laboratories. The concentration of polymer work into a single journal will undoubtedly be welcome to the polymer worker, but the price of the publication (£5 per annum for less than 500 pages) will ensure that it does not occur widely in personal libraries.

P. JOHNSON

W. H. CORCORAN and W. N. LACEY: Introduction to Chemical Engineering Problems. McGraw-Hill, London 1960. 185 pp. 53s. 6d.

M. G. LARIAN: Fundamentals of Chemical Engineering Operations. Constable, London 1960. 644 pp. 62s. 6d.

TEN YEARS ago it was possible to own most of the textbooks in Chemical Engineering which existed, and to be fairly well acquainted with the others. Nowadays they are being published so rapidly that unless complimentary or review copies arrive on one's desk one may never see the newcomers.

Most of these textbooks naturally arise from courses taught at various universities, and each therefore reflects the character of the syllabus and the intellectual atmosphere at a given university. For this reason, the majority are of limited value as aids in teaching elsewhere. Certain of the textbooks published before the flood began achieved widespread recognition ; for instance, *Principles of Chemical Engineering* by WALKER, LEWIS, McADAMS and GILLILAND

of M.I.T. ; *Elements of Chemical Engineering* by BADGER and McCABE of Michigan ; *Chemical Process Principles* by HOUGEN and WATSON of Wisconsin ; and *Chemical Engineering* by COULSON and RICHARDSON of Imperial College ; however, later arrivals have proved less generally useful. Indeed, present tendencies in the teaching of chemical engineering, which stress development from the scientific fundamentals rather than description and analysis of the "unit operations," call for monographs on the principles and applications of chemical and engineering thermodynamics, fluid mechanics, transport processes etc., rather than textbooks which purport to cover the major part of the subject.

It is, in fact, misleading to give a textbook a title which suggests that it deals exhaustively with chemical engineering (unless it confines itself to a superficial survey, or consists of many volumes). Chemical engineering, to my mind, includes chemical thermodynamics and kinetics, fluid mechanics and transfer processes, plant design and a number of other subjects. If a book leaves out some of these subjects its title should reflect the fact.

The book by Professors CORCORAN and LACEY consists of chapters on units, engineering calculations and measurements, behaviour of gases (without reference to fluid mechanics), material and energy balances, introductions to chemical equilibria and kinetics, and the manufacture of ammonia, nitric acid, sulphuric acid and sodium hydroxide. It is concerned principally with the applications of elementary physical chemistry to chemical engineering problems, and not at all with such subjects as fluid mechanics and transfer processes. It would not be possible to guess this from the title.

Probably because of the particular arrangement of the syllabus at the California Institute of Technology, the book is designed "for use before physical chemistry is encountered." There is probably more to be said for this approach to engineering education than would generally be admitted in English universities. The principles of thermodynamics, for instance, are much more difficult than the applications ; should we perhaps start with the simple formulae of thermodynamics and their applications, before returning to the first principles of the subject and developing it in all its rigour ? This method would at any rate re-enact the historical development of thermodynamics, and at the same time make it more digestible to many. Reaction kinetics, as the authors rightly remark, is still (at any rate, from the chemical engineer's viewpoint) an empirical subject, and loses very little by being dealt with as such.

In English circumstances this book might well prove useful when a first-year introductory course in chemical engineering is being taught in parallel with a course in physical chemistry. It is well written, and contains

Book Reviews

over 50 useful examples. Unfortunately, it contains one or two fallacious or misleading statements, particularly with regard to the kinetic basis of equilibrium and the use of activities instead of concentrations in rate equations, which can only store up trouble unless the student is warned against them.

Professor LARIAN's book contains no chemistry; he might claim that the word "operations" in the title should warn us to expect none. Even so, in attempting to cover fluid mechanics, transfer processes and the "unit operations" in some 600 pages, he has shown that one volume is inadequate for the purpose. This would have been a more valuable book, in my opinion, if all fundamentals had been taken as read, and the space available devoted to their application to the "unit operations," and to the description of the principles of operation of various types of equipment. As it is, the treatment of the fundamental principles (e.g. of diffusion) is perfunctory. The author emphasises in his preface that his book has a practical bias. The syllabus at Michigan State University presumably reflects his contention that the graduating engineer "should possess the minimum practical knowledge to qualify for his first job." This is an aim with which one cannot quarrel, although it must be admitted that the graduate who is trained to be *immediately* useful will probably not also have time at the university to master the principles of the subject with sufficient certainty to play a leading part in radically new technological developments. However, there is certainly room in industry for graduates of both kinds; the important thing is that the "practical" course should be as sound, in its own way, as the "intellectual" course. Judged by this criterion, the weakness of Professor LARIAN's book lies in a lack of precision and clarity in his discussion of the fundamentals of such subjects as fluid mechanics and transfer processes. There is no need to be imprecise merely because the discussion remains at the elementary level; in fact it is just at this level that it is important to be crystal clear.

Professor LARIAN is much more successful in his discussion of the general features and the behaviour of various types of equipment, and in his presentation of the conventional methods of calculation; from this point of view the book may prove to be a useful text for the more "practical" type of chemical engineering course, although one would like to see more attention paid to the question of how far the conventional methods can be expected to give the right answer in practice.

P. V. DANCKWERTS

F. RUMFORD: **Chemical Engineering Materials.** (Second Edition) Constable, London 1960. Octavo, 384 pp., 32s. 6d.

THE CHOICE of a material of construction for a chemical plant remains for the most part a matter for experience, and this experience differs in suprising ways from one industry to another. Theory about corrosion helps little, and the body of practical knowledge is vast and not easy to classify. It is, therefore, a pleasure to welcome the second edition of the excellent work on this subject by Dr. RUMFORD, who manages to arrange a wealth of information in a small volume and in such a way that it is easy to discover the properties of a specific material.

The text is divided according to the materials used for construction, and the principal mechanical properties and the resistance to corrosion of each material is discussed. Information is also given on constructional methods and and costs. Metals and inorganic materials, common and uncommon, are treated, and there are preliminary chapters on the mechanism of corrosion and on the testing of materials. (The book by LEE, *Materials of Construction for the Chemical Process Industries*, which is classified according to the chemicals it is desired to contain within the constructional material is complementary to Rumford's book. The two together form a good library on this subject).

In this second edition the author has included more information on the cost of material than in the first edition, and there is a different treatment of the high polymers.

W. SMITH

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